Solvation Chemistry and Reactive Molecules

755. WE-Heraeus-Seminar

17 Sep - 23 Sep 2023

at the Physikzentrum Bad Honnef, Germany

WILHELM UND ELSE
HERAEUS-STIFTUNG

Introduction

The Wilhelm und Else Heraeus-Stiftung is a private foundation that supports research and education in science with an emphasis on physics. It is recognized as Germany's most important private institution funding physics. Some of the activities of the foundation are carried out in close cooperation with the German Physical Society (Deutsche Physikalische Gesellschaft). For detailed information see https://www.we-heraeus-stiftung.de

Aims and scope of the 755. WE-Heraeus-Seminar:

Reactive molecular species such as radicals, polyradicals, carbenes, and molecular ions, play key roles for the understanding of molecular reactivity. Many reactions occur in a solvent environment, and it has been recognized that solvents actively influence reactivity and selectivity of chemical processes rather than being passive bystanders. Due to their high reactivity, most of these species are short-lived, and therefore sophisticated spectroscopic methods have to be used for their characterization. Ultrafast emission and absorption spectroscopy, negative ion photoelectron spectroscopy, matrix isolation spectroscopy, helium nanodroplet spectroscopy, cryogenic tunneling microscopy, among others, are important tools for the characterization of reactive and unusual molecules. The theoretical description of these species using quantum theory is as challenging as the experimental characterization. The highly interdisciplinary seminar will bring together an international group of renowned researchers and young scientists at the beginning of their career from the fields of molecular physics, physical chemistry, physical organic chemistry, material science, theoretical chemistry, and theoretical physics.

The WE-Heraeus-Seminar is part of the ISRIUM (International Conference on Reactive and Unusual Molecules) series of conferences and organized in cooperation with the DFG-funded Cluster of Excellence RESOLV (Ruhr Explores Solvation).

Scientific Organizers:

Prof. Dr. Wolfram Sander	Ruhr-Universität Bochum, Germany E-mail: wolfram.sander@ruhr-uni-bochum.de
Prof. Dr. Elsa Sanchez Garcia	TU Dortmund, Germany E-mail: elsa.sanchez@tu-dortmund.de
Prof. Dr. Martina Havenith-Newen	Ruhr-Universität Bochum, Germany E-mail: Martina.Havenith@ruhr-uni-bochum.de

Introduction

Administrative Organization:

Dr. Stefan Jorda Martina Albert	Wilhelm und Else Heraeus-Stiftung Kurt-Blaum-Platz 1 63450 Hanau, Germany

Phone +49 6181 92325-14
Fax +49 6181 92325-15
E-mail albert@we-heraeus-stiftung.de
Internet: www.we-heraeus-stiftung.de

Venue:

Physikzentrum
Hauptstrasse 5
53604 Bad Honnef, Germany

Conference Phone +49 2224 9010-120

Phone +49 2224 9010-113 or -114 or -117
Fax +49 2224 9010-130
E-mail gomer@pbh.de
Internet www.pbh.de

Taxi Phone +49 2224 2222

Registration:

Martina Albert (WE-Heraeus Foundation)
at the Physikzentrum, reception office
Sunday (14:00 h – 18:00 h)
and Monday (08:00 – 12:30 h)

Program

Program (CET)

Sunday, 17 September 2023

14:00 – 18:00	**Registration**	
Chair		
15:45 – 16:00	Wolfram Sander	**Opening and Welcome**
16:00 – 16:45	Miguel A. Garcia-Garibay	**Strongly Entangled Radical Pairs in Molecular Nanocrystals**
16:45 – 17:05	Hot Topic 1 Jan Philipp Wagner	**Urea-O-Oxides: Criegee Intermediates from N-heterocyclic Carbenes**
17:05 – 17:35	*COFFEE BREAK*	
Chair		
17:35 – 17:55	Hot Topic 2 Artur Mardyukov	**Preparation and Exploration of Heavier Pnictogen Species**
17:55 - 18:40	Karina Morgenstern	**A Local View on the Influence of Solvents on the Reactivity of Surface-Catalyzed Reactions**
18:40 – 20:00	*DINNER*	
Chair		
20:00 – 20:45	Guy Bertrand	**Undressing Carbon**
20:45	**Networking**	

Program (CET)

Monday, 18 September 2023

07:30	*BREAKFAST*	

Chair

08:45 – 09:30	Steven Kass	**Opposites Attract and the Development of Charge-Activated Salts**
09:30 – 10:15	Peter Chen	**Heterobimetallic d8-d10 Complexes as Intermediates, Transition States, and Transition State Analogs for the Transmetalation Step in Cross-Coupling Reactions. Investigations in the Gas Phase, in Silico, in Solution, and in the Solid State**
10:15 – 10:45	*COFFEE BREAK*	

Chair

10:45 – 11:30	Uta Wille	**Phenylalanine Residues are Very Rapidly Damaged by NO3• in an Aqueous Environment**
11:30 – 12:15	Vladimir Popik	**Media Effects on Photo-SPAAC Reaction**
12:15 – 12:35	Martina Havenith	**The Cluster of Excellence RESOLV**

Program (CET)

Monday, 18 September 2023

12:35 – 14:30	*LUNCH*	
Chair		
14:30 – 14:50	Hot Topic 3 Gerhard Schwaab	**Unlike Twins: H-Bonding in H_2S dimer, the "Big Brother" of Water Dimer**
14:50 – 15:35	Cláudio Nunes	**Quantum Tunneling Reactions: Discoveries on the Slippery PES of Arylnitrenes**
15:35 – 16:05	*COFFEE BREAK*	
16:05 – 18:05	**Poster session I**	
18:05 – 19:30	*DINNER*	
19:30	**Networking**	

Program (CET)

Tuesday, 19 September 2023

07:30	*BREAKFAST*	
Chair		
08:45 – 09:30	Benjamin Schwartz	**The Role of the Solvent in Turning Photodissociation into Photoisomerization and in Quantum Decoherence**
09:30 – 10:15	Xijie Wang	**Mapping Fundamental Chemical Processes in Gas & Liquid Using MeV Electrons**
10:15 – 10:45	*COFFEE BREAK*	
Chair		
10:45 – 11:05	Hot Topic 4 Anjali Mahadevan	**2-Isocyanophenylthiyl Radical and its Iodine-triggered Radical Cyclization in Solid Argon**
11:05 – 11:25	Hot Topic 5 Jared King	**Kinetics of the Triplet Excited State of Photoreactive Nanocrystalline 4,4′-Dimethylbenzophenone: Relative Contributions from Intermolecular H-Atom Transfer and Self-Quenching**
11:25 – 12:10	Stefan Grimme	**New 'Low-Cost' Electronic Structure Methods for Large Systems**
12:10 – 12:30	Hot Topic 6 Joel Mieres Perez	**Theoretical Study of Carbenes on Metal Surfaces**

Program (CET)

Tuesday, 19 September 2023

12:30 – 14:25	*LUNCH*	
Chair		
14:25 – 15:10	Peter Schreiner	**The Intrinsic Barrier Width and its Role in Chemical Reactivity**
15:10 – 15:55	Götz Bucher	**Influence of Solvation on Lifetimes of Reactive Quinoid Molecules and Triplet Excited States: Two Case Studies**
15:55 – 16:30	*COFFEE BREAK*	
Chair		
16:30 – 17:15	Patrick Nürnberger	**A Time-Resolved Look on Photochemical Processes for which Adjacent Molecules Play a Crucial Role**
17:15 – 18:00	Hendrik Zipse	**The Stability of O-Centered Radicals**
18:00 – 18:20	Hot Topic 7 Enrique Mendez-Vega	**Taming Unstable Carbocations in Gas-Phase and Water Ice Matrices**
18:20 – 19:55	*DINNER*	
19:55	**Networking**	

Program (CET)

Wednesday, 20 September 2023

07:30	*BREAKFAST*	
Chair		
08:45 – 09:30	Manabu Abe	**Is π-Single Bonding (C–π–C) Possible? A Challenge in Organic Chemistry**
09:30 – 10:15	Igor Alabugin	**Energy of Chemical Bonds as a Driving Force for Organic Reactions: Molecular Springs, Stereoelectronic Frustration, and Electron Upconversion**
10:15 – 10:45	*COFFEE BREAK*	
Chair		
10:45 – 11:30	Viktoria Gessner	**Ligand Exchange at Carbon in Metallated Ylides: Synthetic Entry to Elusive Species**
11:30 – 12:15	Burkhard König	**Generation of Carbanions by Light**
12:15 – 12:35	Hot Topic 8 Takuya Kodama	**Synthesis, Structure, and Reactivity of Tetrylenes Bearing a Phenalenyl-Based Ligand**
12:35 – 14:00	*LUNCH*	
14:05 – 14:15	***Conference Photo*** ***(in the front of the main entrance, before departure to Excursion)***	
14:15 – 22:15	**Excursion and Dinner**	

Program (CET)

Thursday, 21 September 2023

07:30	*BREAKFAST*	
Chair		
08:45 – 09:30	Holger Bettinger	**Access to and Properties of the Strained Heteroaromatic Benzoborirene Motif**
09:30 – 10:15	Fabien Borget	**Interstellar Iced Solvation - from Laboratory Studies to a Space Mission Instrument Conception**
10:15 – 10:45	*COFFEE BREAK*	
Chair		
10:45 – 11:30	Yuan-Pern Lee	**Reactive Molecules Investigated with Para-Hydrogen Infrared Matrix Spectroscopy**
11:30 – 12:15	Murthy Gudipati	**Solvation of Electrons, Ions, and Organics in Astrophysical and Planetary Ices**
12:15 – 12:35	Hot Topic 9 André Eckhardt	**Spectroscopic Characterization of Interstellar Relevant Imine Species**

Program (CET)

Thursday, 21 September 2023

12:35 – 14:30	*LUNCH*	
Chair		
14:30 – 15:15	Christian Merten	**VCD Spectroscopy Under Cryogenic Conditions: Of Matrix Effects and Photochemistry of Chiral Molecules**
15:15 – 16:00	Henrik Ottosson	**Excited State Aromaticity and Antiaromaticity: From Scopes to Pitfalls**
16:00 – 16:45	Takashi Kubo	**Recent Studies on π-Expanded Trinaphtho[3.3.3]propellane**
16:45 -18:30	**Poster session II**	
18:30 - 20:00	*DINNER*	
20:00	**Networking**	

Program (CET)

Friday, 22 September 2023

07:30	*BREAKFAST*	
Chair		
08:45 – 09:30	Anna Gudmundsdottir	**Turning off and On Photodynamic Behavior of Organic Azide Crystals**
09:30 – 10:15	Gary Douberly	**Tba**
10:15 – 10:45	*COFFEE BREAK*	
Chair		
10:45 – 11:30	Patrick Hemberger	**Ketenes in Heterogeneous Catalysis: Blessing or Course?**
11:30 – 12:15	Udo Brinker	**Carbene 1,3-C–H Bond Insertion Reactions: Potential Sources of Cyclopropatetrahedrane**
12:15 – 13:00	Dean Tantillo	**Dynamic Effects on Selectivity of Organic Reactions in Solvent**
13:00 – 14:30	*LUNCH*	
Chair		
14:30 – 15:15	Josef Michl	**Porphene and Porphite: Porphyrin Analogs of Graphene and Graphite**
15:15 – 16:00	Dominik Munz	**A Plumba Triplet Carbene**

Program (CET)

Friday, 22 September 2023

16:00 – 16:30	*COFFEE BREAK*	
Chair		
16:30 – 17:15	Rainer Herges	**Early Detection of Cancer by Metabolic Imaging**
17:15 – 17:45	Scientific Organizers	**Poster Prize Awards & Closing Remarks**
17:45	*HERAEUS DINNER* *(social event with cold & warm buffet and complimentary drinks)*	

Saturday, 23 September 2023

08:00	*BREAKFAST*

End of the seminar and departure

NO DINNER for participants leaving on Sunday! A self-catering breakfast will be provided on Sunday.

Posters

Posters

Jama Ariai	**The Entropic Penalty for Associative Reactions and their Physical Treatment during Routine Computations**
Frederike Beyer	**Nitrenes and Chirality in Cryogenic Matrices**
Jun-Ying Feng	**Infrared Spectra of Isomers of Protonated and Hydrogenated Phenanthrene Isolated in Solid Para-Hydrogen**
Vincent George	**Photogenerated Donor-Donor Diazo Compounds Enable Facile Access to Spirocyclopropanes**
Stefan Henkel	**Hydrogen Bonding and Tunnling in $H_2O \cdots H_2S$ Clusters**
Ku Kajikawa	**SOMO-HOMO Conversion of Radical Species within the CPP Structure**
Ginny Karir	**Generation, Photoionization, and Reactivity of Phenylethynyl Radical – Insights into Interstellar Chemistry**
Piyush Kumar	**Photochemistry of 2-Iodoimidazole: A Computational and Matrix Isolation Infrared Spectroscopic Studies**
Arunlibertsen Lawzer	**Free Ethynylpnictinidenes: Matrix Isolation and Spectroscopic Studies**
Serhii Medvedko	**Synthesis of Thiourea S-Oxides via Formal SO Transfer from Thiirane Oxides**
Walimuni Dinindu Mendis	**Exploring Photoreactivity and Photodynamic Behavior of (1-azidoethene-1,2-diyl)dibenzene and 2,3-diphenyl-2H-azirine**

Posters

Philipp Meyer	**Reaction of Lithium Hexamethyldisilazide (LiHMDS) with Water at Ultracold Conditions**
Maurice Niehoff	**Synthesis and Reactivity of Fluorinated Terphenyl Nitrenes Beyond Cryogenic Conditions**
Adrián Portela Gonzáles	**Stability of Triplet Arylnitrenes in Nafion Polymer at Ambient Temperatures**
Melania Prado Merini	**Heavy-Atom Tunneling in Bicyclo[4.1.0]hepta-2,4,6-trienes**
Weiyu Qian	**In Pursuit of Low-Valent Pnictogen Species**
Julien Rowen	**Investigation of Fluorenyl-Based Reactive Intermediates**
Mayank Saraswat	**Gas Phase Thermal Rearrangement of Astrochemical Relevant Species: Threshold Photoelectron and Matrix Isolation Spectroscopic Study**
Shubhra Sarkar	**Radical Anions: Carbonyl versus Cyano Compounds**
Niklas Sülzner	**Going Beyond Implicit Solvent Effects on Hydroxypyrene Photoacids**
Fiona Wasson	**Organic Hydroperoxide Triplet Reactivity for Releasing O_2 Utilizing Photochemical Reactions**
Lilith Wohlfart	**Investigating the Photodissociation Dynamics of CH_2Br with VMI**
Liu Yining	**Theoretical Study of the Cyclopentadienylidene Carbene and its Reactivity on Metal Surfaces**

Abstracts of Lectures

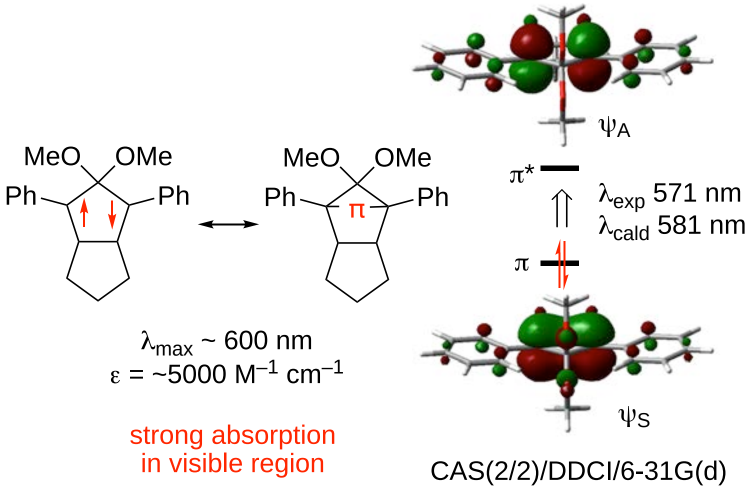
(in alphabetical order)

Is π-Single Bonding (C–π–C) Possible? A Challenge in Organic Chemistry

M. Abe

Department of Chemistry, Hiroshima University, Higashi-Hiroshima City, Japan
E-mail: mabe@hiroshima-u.ac.jp

Chemical bonding systems determine the nature of molecules. In organic chemistry, there are two bonding types for carbon–carbon connections: σ-bonding and π-bonding. In this presentation, several aspects of studies in the last two decades addressing a naive question "Is π-single bonding (C–π–C) possible?" will be presented: (1) features of π-single bonded species; (2) molecular design for π-single bonding; (3) generation and detection of singlet diradicaloids with a π-single bonding character; (4) future prospects of π-single bonded species.



Energy of chemical bonds as a driving force for organic reactions: molecular springs, stereoelectronic frustration, and electron upconversion

Igor V. Alabugin

Department of Chemistry and Biochemistry,
Florida State University, Tallahassee, Fl, USA

Molecules store energy and, as bonds are formed and broken, every chemical process can either store or release energy. This talk will discuss practical ways for incorporating this common knowledge into reaction design and in searching for new physical phenomena.

After outlining the interplay of kinetics with thermodynamics and the special role of weak bonds in catalysis, I will discuss how much energy can one store in common functional groups, introduce the familiar textbook functionalities that accumulate more energy than an excited state, and show how O-O bonds can rival C-C bonds as building block for creating complex polycyclic organic molecules.

I will show that the key to controlling the flow of energy in chemical reactions is in using unique stereoelectronic features of each functionality and in coupling unfavorable and favorable elementary steps in a chain of chemical transformations.

In the final part, I will introduce the phenomenon of electron upconversion, a counterintuitive way to transform weak reductants into strong reductants in a thermodynamically favorable fashion. Such processes enable electrocatalytic transformations where a single electron can drive multiple catalytic cycles.

References

Alkyne Origami: Folding Oligoalkynes into Polyaromatics. I. V. Alabugin, E. Gonzalez-Rodriguez. *Acc. Chem. Res.,* **2018**, *51*, 1206.

Stereoelectronic Power of Oxygen in Control of Chemical Reactivity: the Anomeric Effect is not Alone. I. V. Alabugin, L. Kuhn, M. G. Medvedev, N. V. Krivoshchapov, V. A. Vil', I. A. Yaremenko, P. Mehaffy, M. Yarie, A. O. Terent'ev, M.A. Zolfigol. *Chem. Soc. Rev.* **2021**, *50*, 1025.

Testing the Limits of Radical-Anionic CH-Amination: a 10-Million-Fold Decrease in Basicity Opens a New Path to Hydroxyisoindolines via a Mixed C-N/C-O-Forming Cascade. Q. Elliott, G. Gomes, C. J. Evoniuk, I. V. Alabugin, *Chem. Science*, **2020**, *11*, 6539.

Upconversion of Reductants. M. A. Syroeshkin, F. Kuriakose, E. A. Saverina, V. A. Timofeeva, M. P. Egorov, I. V. Alabugin. *Angew. Chem. Int. Ed*., **2019**, *58,* 5532.

Undressing Carbon

G. Bertrand

UCSD-CNRS Joint Research Chemistry Laboratory (IRL 3555), Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, California 92093-0358, United States

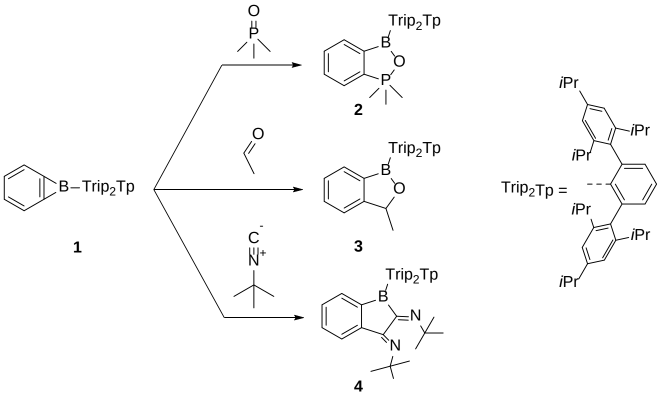
Since the discovery at the beginning of the XXth century of a stable radical, many species that do not obey the octet rule have been isolated. The availability of these stable versions has led to a variety of applications. This statement is well supported by the example of stable carbenes, with only six-valence electrons, which have become among the most powerful tools in chemistry. To push the boundaries further, we wish to undress carbon atoms even more. As an illustration we will discuss our results dealing with a dicoordinate carbodication, which according the Gutmann-Beckett scale is more Lewis acidic than any known boron species.

Access to and properties of the strained heteroaromatic benzoborirene motif

Holger F. Bettinger[1]

[1]*Institut für Organische Chemie, Universität Tübingen, Tübingen, Germany*

The fusion of a three-membered borirene ring with benzene results in benzoborirenes. This class of heterocycles combines high strain with aromatic stabilization, and hence can be a testing ground for probing bonding theories.[1-2] Benzoborirene was first inferred from crossed-molecular beams experiments[3-5] before matrix isolation techniques could provide spectroscopic evidence for their existence.[6-7] The electrophilic boron center along with the strained scaffold not only presents challenges to the conventional synthesis of benzoborirenes,[8-10] but it also provides the opportunity to access unusual boron containing heterocycles. We here report the interaction of a kinetically stabilized benzoborirene **1** with a number small molecules featuring double bonds.



References

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[6] H. F. Bettinger, Chem. Commun. 2756 (2005)
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[9] H. Zhang, J. Wang, W. Yang, L. Xiang, W. Sun, W. Ming, Y. Li, Z. Lin, Q. Ye, J. Am. Chem. Soc. **142**, 17243 (2020)
[10] M. Sindlinger, M. Ströbele, C. Maichle-Mössmer, H. F. Bettinger, Chem. Commun. **58**, 2818 (2022)

Interstellar iced solvation - from laboratory studies to a space mission instrument conception.

F. Borget[1]

[1]Aix-Marseille Université, CNRS, PIIM, Marseille, France

In this presentation, I will discuss the latest findings regarding the detection of radicals [1,2] within simulated interstellar ices. These investigations provide crucial insights into the mechanisms underlying the formation of essential Interstellar Complex Organic Molecules (iCOM). This, in turn, sheds light on the creation of prebiotic molecules across various objects such as nebulas, icy planets, comets, asteroids... A particular emphasis will be placed on the exploration of potential intermediates that play a role in interstellar chemical pathways [3].

Drawing from our laboratory simulations, we have developed a prototype experiment known as ProbICE that I will describe. This innovative instrument is poised to take part in future space missions and is designed to track the progression of complex ices under the direct influence of "natural" solar radiation in low orbit missions. Additionally, ProbICE offers a unique opportunity to capture on-site samples of ices, serving as a steppingstone for upcoming ambitious missions dedicated to the comprehensive study of icy objects within our solar system.

References

[1] Gutiérrez-Quintanilla, A.; Layssac, Y.; Butscher, T.; Henkel, S.; Tsegaw, Y. A.; Grote, D.; Sander, W.; Borget, F.; Chiavassa, T.; Duvernay, F. *Mon. Not. R. Astron. Soc.* **2021**, *506* (3), 3734–3750. https://doi.org/10.1093/mnras/stab1850.

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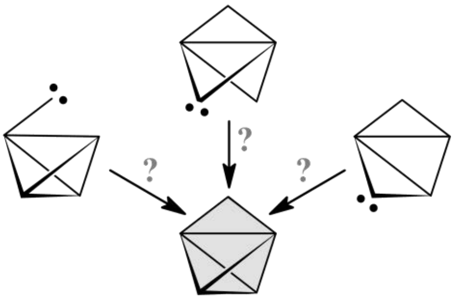
Carbene 1,3-C−H Bond Insertion Reactions: Potential Sources of Cyclopropatetrahedrane

M. G. Rosenberg[1] and U. H. Brinker[1,2]

[1] Department of Chemistry, The State University of New York at Binghamton, P. O. Box 6000, Binghamton, NY 13902-6000, United States
[2] Institute of Organic Chemistry, University of Vienna, Währinger Strasse 38, 1090 Vienna, Austria



Cyclopropatetrahedrane is a hypothetical polycycloalkane with multiple fused cyclopropanes that imbue it with phenomenal strain.[1,2] Nevertheless, the structure may ultimately be formed by intramolecular cyclopropanation—a *signature* carbene reaction—within suitable carbene precursors. A carbene's divalent C atom forms three-membered rings by either inserting into an aligned γ-C−H bond or adding to a nearby C−C double bond. Computational chemistry was used to study three H-atom transfer reactions and a cycloaddition was also computed. The ωB97X-D/cc-pVTZ theoretical model was used to compute the equilibrium geometries of four carbene candidates; single-point energies were computed using coupled-cluster theory. A transition state was found for the four carbene elementary steps under study and intrinsic reaction coordinate computations could be obtained for each one. The results support the hypothesis that each carbene is directly linked to cyclopropatetrahedrane. Kinetic isotope effects (k_H/k_D) for the three H/D-atom-transfer steps were computed to further characterize the 1,3-C−H bond insertion reactions. (Tetrahedryl)carbene was examined closely because it has an inverted C atom. The carbene's distorted shape is due to significant C−C bond hyperconjugation, as in (cyclobutyl)carbene.[3] The molecular orbitals of both cyclopropylidenes were studied with deference to rearrangement.[4]

References

[1] M. G. Rosenberg, U. H. Brinker, *J. Org. Chem.* **87**, 16902 (2022).
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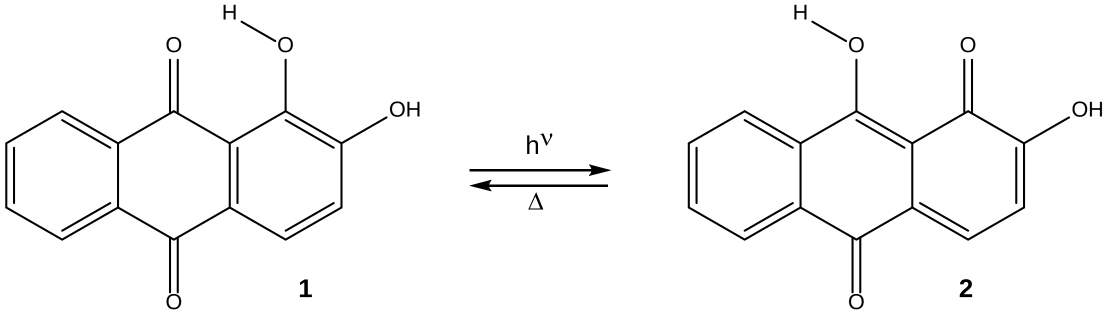
Influence of Solvation on Lifetimes of Reactive Quinoid Molecules and Triplet Excited States: Two Case Studies

Götz Bucher[1]

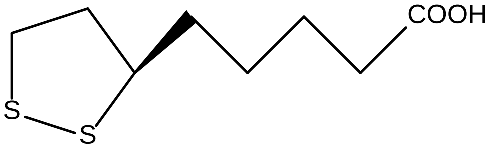
[1]*School of Chemistry, University of Glasgow, Joseph-Black-Building,*
University Avenue, Glasgow G12 8QQ

The lifetimes of reactive intermediates and excited states can be significantly influenced by interaction with solvent molecules. The presentation will give two examples where interaction with solvent (or co-solvent) molecules either significantly extends the lifetime of a reactive intermediate or shortens the lifetime of a triplet excited state.

Alizarin **1** is a well-known member of the class of hydroxyanthraquinone dyes that – in a mixture with related compounds – has been used as dyestuff since ancient times. It is highly photostable. In spite of this photostability, weak transients are observed by ns Laser Flash Photolysis. By means of DFT calculations, I assign the transient observed to an isomeric quinone **2**. The discrepancy between the expected lifetime of **2** (extremely short!) and its experimental lifetime (tens to hundreds of μs, depending on the solvent) will be discussed in the presentation.



Lipoic acid **3** is an important biomolecule. When studying its photochemistry, we were surprised to learn that its (σ*,π*) triplet excited state is quenched by water.[1] The mechanism of this quenching will be discussed. I will also present the results of high-level calculations on the structures of exciplexes of a simpler triplet excited state, triplet formaldehyde **4**, with water and other reaction partners.



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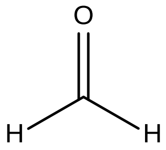

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Heterobimetallic d^8-d^{10} complexes as intermediates, transition states, and transition state analogs for the transmetalation step in cross-coupling reactions. Investigations in the gas phase, in silico, in solution, and in the solid state

Prof. Dr. Peter Chen
Laboratorium für Organische Chemie, ETH Zürich
Vladimir-Prelog-Weg 2, 8093 Zürich, Switzerland
peter.chen@org.chem.ethz.ch

We report an experimental study, with accompanying DFT calculations, on a series of heterobimetallic complexes featuring Pd(II) or Pt(II), paired with Cu(I), Ag(I), Au(I) or Zn(II). The isolable complexes, for which we have extensive structural data in the solid state, in solution, and in the gas phase, are models for the intermediates and transition state for the transmetalation step in Sonagashira and Negishi coupling reactions, among which, according to the DFT calculations, only the transition state has the two metal centers within bonding distance. The d^8-d^{10} metal-metal interaction, variously attributed to electrostatic, orbital, or dispersion effects, has been proposed to be a stabilizing factor lowering the transition state for transmetalation, which naturally then becomes relevant to cross-coupling by shifting the turnover-limiting step to one of the other elementary reactions in the catalytic cycle. We use the well-defined heterobimetallic complexes to explore the strength of the interaction. We let a molecule choose between alternative structures, with or without a metal-metal interaction. We investigate dissociation reactions to distinguishable products, again, starting from a well-defined heterobimetallic complex. We measure absolute binding energies in the gas phase and in solution. Analysis of the structures in the solid state and in solution, a competitive dissociation experiment in the gas phase, and an independent gas-phase measurement of non-covalent interactions under conditions of controlled geometry, indicate that the dispersion-corrected DFT methods used in the study appears to overestimate the strength of the interaction in many cases, but not always, usually distorting the shape of the computed potential energy surface systematically for transmetalation.

Spectroscopic Characterization of Interstellar Relevant Imine Species

Vladimir D. Drabkin, Viktor Paczelt, and André K. Eckhardt

Lehrstuhl für Organische Chemie II, Ruhr-University Bochum, Germany

Simple imines are frequently used as building blocks in the synthesis of more complex molecules. In solution imines are typically prepared from carbonyl compounds and ammonia or primary amines, respectively. The simplest aldimine, formaldimine (H_2CNH), has been discovered in space but cannot be isolated on Earth due to polymerization or oligomerization when concentrated. Aldimine building blocks play a key role in the formation of biorelevant molecules like amino acids or nucleobases in prebiotic chemistry. However, spectroscopic data of the compound class are rare or missing at all due to their high reactivity and the absence of molecular precursors for an on-demand mild generation. The overall goal of this project is to learn more about interstellar and prebiotic imine chemistry and characterize often proposed but yet elusive imine species.

1,2-Diiminoethane was photochemically prepared from explosive 1,2-diazidoethane in solid argon at 3 K and characterized by infrared and UV/Vis spectroscopy. In aqueous solution the simplest diimine serves as a fundamental building block for imidazole heterocycles.

The simplest *α*-imino acid, namely glycine imine, was prepared by UV irradiation of azidoacetic acid in solid argon at 3 K and characterized by IR and UV/Vis spectroscopy. In aqueous solution at higher concentrations glycine imine undergoes self-reduction to glycine by oxidative decarboxylation chemistry. The imine serves a critical intermediate in prebiotic amino acid synthesis. In the future the solvation and hydrolysis of imines will be studied in low-density amorphous water ice.

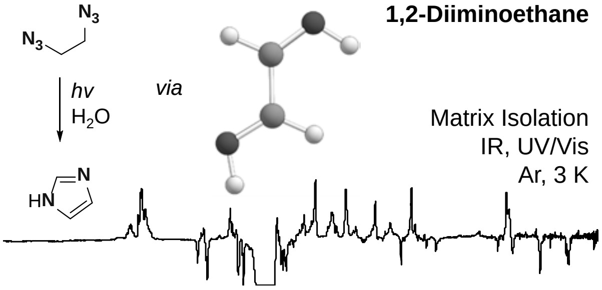

Figure 1: Spectroscopic characterization 1,2-diiminoethane by photolysis of explosive 1,2-diazidoethane in solid argon at 3 K.

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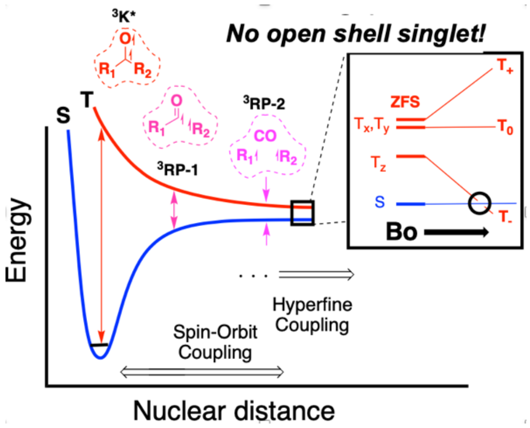
Strongly Entangled Radical Pairs in Molecular Nanocrystals

Miguel A. Garcia-Garibay

Department of Chemistry, University of California, Los Angeles CA, USA

While crystals present unique opportunities to control and understand photochemical reactivity, the use of transient kinetics and spectroscopy has been challenging due to their complex optical properties. However, we recently showed that problems arising from their high scattering, large optical densities, birefringence, and dichroism can be overcome with aqueous suspensions of nanocrystals of the same order of magnitude as the light used for excitation [1]. Using pump-probe methods with pulsed laser excitation demonstrates that triplet acyl-alkyl radical pairs generated within the constraints of their nano-crystalline ketone precursors are a promising platform for repeated generation of spin qubit pairs with potential applications in quantum information science. In this lecture we report the photochemistry and transient spectroscopy of a series of nano-crystalline ketones that can generate strongly entangled triplet radical pairs that are forced to remain static and within bonding distances [2]. We propose that triplet radical pairs with unprecedented long lifetimes are the result of the short inter-radical distances and the co-linear orientation of the two singly occupied orbitals, which are expected to result in large singlet-triplet energy gaps, large zero-field splitting parameters, a poor geometry for spin-obit coupling, and limited spin-lattice relaxation. Notably, a subset of these ketones generates radical pairs which demonstrate promising performance along multiple dimensions crucial for quantum information science.



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Ligand Exchange at Carbon in Metallated Ylides: Synthetic Entry to Elusive Species

Viktoria H. Gessner[1] **and the Gessner Group**

[1] Faculty of Chemistry and Biochemistry, Ruhr-University Bochum, Universitaetsstr. 150, 44801 Bochum, Germany. Twitter: @ViktoriaGessner, Web: https://www.gessnerlab.rub.de/; Email: viktoria.gessner@rub.de

Phosphines are amongst the most important ligands in coordination chemistry and frequently applied in transition metal catalysis. Here, they often are readily displaced by other ligands which subsequently participate in the bond forming step within the catalytic cycle. Owing their unique electronic structure, it was recently shown that also ylidic phosphorus compounds such as carbodiphosphoranes[1] can be interpreted as coordination complexes of carbon. However, this bonding situation has so far rarely been used to enable access to new compounds via a formal ligand exchange at carbon.

In the past years, our group has reported on the synthesis and reactivity of α-metallated ylides (**1**). Owing to their highly nucleophilic character these compounds turned out to be excellent precursors to access electron-rich phosphines with beneficial properties for homogeneous catalysis[2] and to stabilize electron-deficient main group species.[3] Most recently however, we uncovered that metallated ylides can also react as coordination complexes of carbon to readily exchange the phosphine substituent by carbon monoxide.[4] This remarkable reactivity provided access to ketenyl anions **2** which have long been regarded as elusive species, but proven sufficiently stable to serve as starting materials to ketenes and a variety of carbonyl compounds. Here, we will summarize this unique reactivity of metallated ylides.

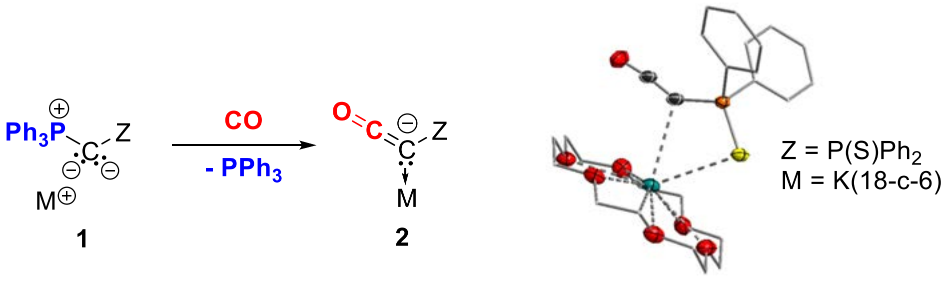

Figure 1. Phosphine by CO exchange in metallated ylides.

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New ’low-cost’ electronic structure methods for large systems

Stefan Grimme

Mulliken Center for Theoretical Chemistry, Clausius Institute for Physical and Theoretical Chemistry, University of Bonn, Beringstraße 4, 53115 Bonn, Germany

All widely used semi-empirical quantum chemical methods like PM6, DFTB, or GFN-xTB are formulated in a (almost) minimal basis set of atomic orbitals, which limits the achievable ac- curacy for many important chemical properties. Recently, we proposed a new special purpose tight-binding (TB) electronic Hamiltonian termed PTB[1] which is expressed in an accurate po- larized valence double-zeta AO basis set (vDZP). The basis has been specially optimized in molecular DFT calculations using standard ECPs for all elements up to radon[2]. The PTB method aims primarily at reproducing the one-particle density matrix of a DFT reference cal- culation with the ωB97X-V range-separated hybrid (RSH) density functional[3] in exactly the same AO basis. The combination of ωB97X(-V) with vDZP/ECP and an adjusted D4 disper- sion correction defines a new member in our hierarchy of efficient composite electronic structure methods, termed ωB97X-3c[2] and is used as reference. The basis set optimization concept is furthermore applied to a minimal set of AOs which is – as a totally new ingredient – made adap- tive, i.e., radially different for symmetry distinct atoms in a molecule. This q-vSZP set forms the basis of our third-generation tight-binding model GP3-xTB which includes non-local Fock- exchange as well as other new Hamiltonian terms. It aims at general purpose (GP) applicability in chemistry and more closely approaches DFT accuracy than previous semi-empirical meth- ods at only slightly increased computational cost. When the number of primitive Gaussians in q-vSZP is somewhat reduced, and this basis is coupled with an RSH and atomic correction po- tentials (ACP), an extremely efficient new 3c-composite method dubbed ωB97M-3c is obtained.

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Solvation of Electrons, Ions, and Organics in Astrophysical and Planetary Ices

Murthy S. Gudipati[1]

[1]Science Division, Jet Propulsion Laboratory, California Institute of Technology,
Pasadena, CA 91109, USA

Water (H_2O) is ubiquitous throughout the Universe in the gas, liquid, and solid (ice) forms [1]. Liquid water is one of the essential components for life to sustain and thrive on Earth. One of the theories of the origin of life on Earth is that the prebiotic molecules of life were delivered to Earth by comets and asteroids that bombarded Earth around 4 billion years ago. Kuiper Belt Objects (KBOs) and Oort Cloud that are the reservoirs of comets are the coldest water-rich icy bodies in our solar system. These icy bodies of a few meters to a few tens of kilometers size are the leftover and unaltered material during the protoplanetary phase of our solar system formation. Hence, it is understood that cometary nuclei are composed of primordial water-ice and trapped complex organic molecules that were synthesized by stellar radiation and cosmic rays from simple molecules consisting of C, H, N, O elements (such as CH_4, CO, CO_2, NH_3, CH_3OH, etc). Thus, understanding how water ice and simple organics evolve under radiation environment is one of the key steps to bring us closer to understand origin of life on Earth.

Amorphous water-ice, which is a metastable phase, is a unique medium that has high electronegativity, stabilizes charged species, has minimal effect on the electronic and vibrational spectral properties of trapped species [2-5]. Crystalline water-ice is less prone to interact with other molecules, particularly non-hydrogen bonding and non-polar. In this talk I will summarize our research over the past two decades on solvation of electrons, ions, and organics in astrophysical and planetary ices.

Acknowledgments: The research presented here was funded by NASA Research and Analysis Programs such as Solar System Workings (SSW), Habitable Worlds (HW), Discovery Data Analysis Program (DDAP), and was carried out at the Jet Propulsion Laboratory, California Institute of Technology, under a contract with the National Aeronautics and Space Administration (NASA).

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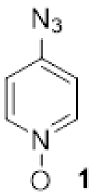
Turning on and off Photodynamic Behavior of Organic Azido Crystals

Fiona Wasson,[1] James Poole,[2] Upasana Banerjee,[1] Raj Merugu[1] and Anna D. Gudmundsdottir[1]

[1]*University of Cincinnati, Cincinnati, OH USA*
[2]*St Cloud State, St Cloud, University, MN*

Recent findings highlight that organic crystals can be flexible when subjected to external stimuli, such light or heat, as they can bend, curl, hop, or fragment.[1] Thus, photodynamic crystals can convert light into mechanical energy, and therefore they have a potential use in the fabrication of mechanically-tuneable components for actuation, energy harvesting, flexible electronics, and switchable reflectors. In addition, such crystals can be used as sensors and probes. Irradiation of crystalline azido compounds results in release of N_2 gas, that can cause photodynamic response of the azido crystals.[2] Herein, we present that the photolysis of azido crystals (**1**) that only undergo only a surface reaction to from azo dimers, and the crystals are remarkable stable and can therefore be used for photolithography applications, as demonstrated with confocal and digital microscopy, and SEM. The surface reactivity of the crystals was characterized by confocal Raman microscopy. Similarly, irradiation of crystals of azide **2** also results in only surface reaction, to form **3** and release of N_2 gas. Digital microscopy shows that the crystals of **2** crack in specific directions, but the crystals stay intact. In contrast, mixed crystals of **2** and **4** display different photodynamic behaviour, as the mixed crystals do not crack in a specific direction, whereas crystals of **4** do not show any photoreactivity or photodynamic behaviour. We will discuss what factors render azido crystals photodynamic.



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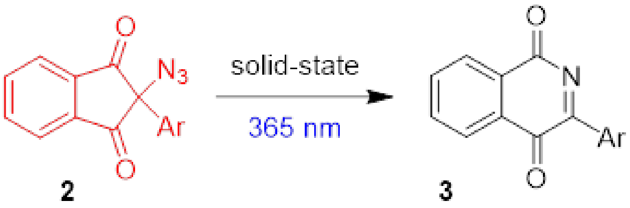
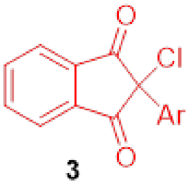


2 **3**



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RESOLV – Ruhr Explores Solvation

Martina Havenith-Newen
Ruhr-Universität Bochum, Germany

Since 2012, the Cluster of Excellence RESOLV has been at the forefront of pioneering Solvation Science as an interdisciplinary field, providing a unified framework to comprehend solvation processes. As most chemical and biological reactions occur in solutions, the role of solvents became a pressing question. Depart from the conventional view of solvents as inert mediums, RESOLV considers solvents as active participants in a reaction.

Funded with 72 million EUR from the German Federal Government and the state of North Rhine-Westphalia since 2012, RESOLV's research has uncovered intriguing challenges within Solvation Science. With about 200 scientists from the Ruhr University Bochum, the TU Dortmund University and four other institutions in the German Ruhr area as well as over 20 international partner institutions worldwide, RESOLV fosters open, inter- and transdisciplinary collaborations amongst physicists, chemists, and biologists, akin to disciplines such as Materials Science or Neuroscience.

RESOLV’s research is organized into three core areas:

Area I: Currently, key concepts in Solvation Science are firmly established in terms of global properties of homogeneous bulk systems at thermodynamic equilibrium conditions. However, it is intriguing to see how local solvation phenomena in nanoheterogeneous environments determine the reactivity and selectivity in solution as well as the function of electrocatalysts, receptors, and enzymes.

Area II: Solutes imprint their shape (molecular structure, charge distribution) on the surrounding solvent shells, thus creating solvent arrangements that both in structure and dynamics deviate from the bulk. This so-called ‘solvent shaping’ in the vicinity of reaction centres, whether an enzyme or a catalytic encounter complex, has emerged as an underlying theme to enable the optimization of both yield and selectivity.

Area III: Restricted solvation on surfaces, chemical reactivity in nanoconfined water, pressure modulation of reactivity and phase behaviour, and cryochemistry are all linked by a single concept: ‘Stressed solvent’. The notion of a stressed solvent implies the tuning of solvent properties and function without changing the solvent itself. Therefore, in this area, we consider high pressure, low temperature, and strong confinement as key stressors that enable us to rigorously modulate solvation properties without changing the chemical identity of the solvent.

RESOLV utilizes advanced laser spectroscopy, microscopy, synthesis, and theory to study and manipulate molecular-level solvation. This research is essential to advance technologies that could reuse CO_2 for chemicals production or increase the efficiency of energy conversion.

RESOLV established a Solvation Science faculty and a graduate school of Solvation Science and implanted measures to foster gender and diversity.

Ketenes in Heterogeneous Catalysis: Blessing or Course?

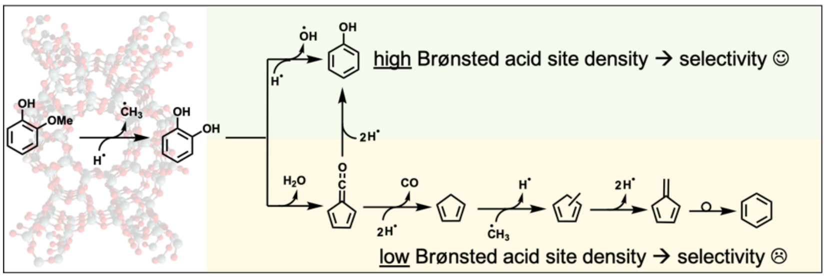
Patrick Hemberger[1]

[1]*Paul Scherrer Institute, Villigen PSI, Switzerland*

Ketenes are popular synthons in organic chemistry, due to their high reactivity. They are utilized as electrophiles as well as in cycloaddition reactions. Their role in heterogeneous catalytic reactions has only recently been brought into spotlight, however due to their high reactivity, direct detection with GC/MS or NMR is not feasible. If we understand the formation and fate of ketenes, we can unveil the chemistry behind the reactive systems and can actively take control of the catalytic process.

In this talk, we will introduce photoelectron photoion coincidence spectroscopy (PEPICO) with vacuum ultraviolet synchrotron radiation from the Swiss Light Source (SLS) as a versatile tool to investigate the mechanisms of heterogeneous catalytic reactions. PEPICO combines both mass spectrometry and photoelectron spectroscopy as a reaction microscope to isomer-selectively detect highly reactive and elusive intermediates including ketenes and radicals.

We will discuss how this state-of-the-art detection tool gained new insights into catalytic fast pyrolysis (CFP) of lignin model compounds, such as methoxyphenols and benzenediols, over different zeolites. The reaction of guaiacol is initiated by a demethylation to yield catechol (*ortho*-dihydroxybenzene), which can uniquely dehydrate to form the reactive fulvenone ketene intermediate (c-$C_5H_4=C=O$, orange route). This ketene rapidly forms phenol or yields cyclopentadiene upon decarbonylation (orange route). Due to the high reactivity of the ketene, the reaction is very unselective and yields multiple products, besides phenol. In addition to the fulvenone pathway, a direct dehydroxylation reaction (green route) to phenol can take place, depending on the availability of Brønsted acid sites. By lowering the Si/Al ratio in the faujasite catalyst, we increased the Brønsted acid site density, which suppresses the fulvenone ketene formation and leads to a phenol selectivity increase by a factor of 5, rendering ketenes as unwanted intermediates during lignin catalytic pyrolysis.



If time permits, we will switch gears to the methanol-to-olefin process shining new light on the initiation of this zeolite catalyzed process. We will show strong evidence that the simplest ketene ($H_2=C=O$), ethenone, is responsible for the formation of the first olefins.

Early Detection of Cancer by Metabolic Imaging

R. Herges

Institute for Organic Chemistry, Kiel, Germany

The transition of a healthy cell to a cancer cell starts with the change of energy metabolism long before the cells proliferate uncontrollably and lead to anatomical changes (tumors, metastases) that can be visualized by conventional imaging. In particular, lactate/pyruvate metabolism is considered a hall-mark for cancer (Warburg effect). To detect cancer by metabolic imaging the sensitivity of magnetic resonance imaging (MRI) has to be increased by at least 5 orders of magnitude. This cannot be achieved by increasing the magnetic field strength. Hyperpolarization is currently the only method to achieve the necessary signal-to-noise ratio. The most commonly used method at present is DNP (dynamic nuclear polarization). For this, the sample (pyruvate) together with an organic radical is cooled to <1K in a strong magnetic field and irradiated with microwaves for about 2h to transfer the hyperpolarization of the electrons to that of ^{13}C. The hyperpolarization has a half-life (T_1 time) of ˜2 min. The sample is then very quickly warmed to room temperature and injected into the patient. Several clinical studies have shown that this approach can be used to reliably detect prostate cancer and other types of cancer at a very early stage. However, the DNP method is so laborious and expensive that it is unlikely to find its way into clinical practice.

We take a different, much simpler approach to hyperpolarization. We use the spin order of para-hydrogen, transfer it as hyperpolarization to the 13C in 1-position of vinyl pyruvate, hydrolyze the ester and obtain hyperpolarized pyruvate. The process is much faster, simpler and less complex than DNP. We achieve hyperpolarization of up to 30%, which is sufficient for metabolic MRI.

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Opposites attract and the development of charge-activated salts

S. Dempsey,[1] X. Wang,[2] and S. Kass[1]

[1]*University of Minnesota, Department of Chemistry, Minneapolis, MN, USA*
[2] *Physical Sciences Division, Pacific Northwest National Laboratory, Richland, Washington, USA*

Opposites attract and this can be exploited in organocatalysis by incorporating a positively charged center into a hydrogen bond donor or alternatively a Brønsted or Lewis acid so as to afford a charge-activated catalyst.[1,2] This approach has been exploited with a variety of substrates (e.g., thioureas, BINOL-phosphoric acids, TADDOLs, and metallocenium derivatives) and it seems rather obvious that it should work equally well for producing charge-activated bases and nucleophiles by incorporating a negatively charged substituent into a neutral base/nucleophile since opposites attract. To our surprise, our initial efforts at producing more reactive nucleophiles/bases were unsuccessful. This is because the key to forming a charge-activated acid/electrophile or base/nucleophile is to pair the charged reagent with a weakly coordinating anion (WCA) or cation (WCC), but whereas the former species have been extensively investigated the latter are underdeveloped.[3]

In this presentation recent efforts to character and develop WCCs to produce charge-activated bases/nucleophiles will be discussed. A series of commonly used weakly coordinating cations (WCCs) are evaluated, and surprisingly simple substituted tetraarylphosphonium ions were found to be as good or better than P2 and P5 phosphazenium ions. A variety of electrostatically enhanced 3- and 4-pyridylborate salt catalysts also will be discussed. These substrates show significant improvement over an activated non-charged reference compound in both a stoichiometric S_N2 reaction and a base-catalyzed urethane synthesis.

Characterization of the salts by a number of means (e.g., ion-pairing equilibrium constant determinations, conductivity measurements, DOSY NMR) indicate that ion-pairs and aggregation are important. Gas-phase vertical detachment energies, however, are found to linearly correlate with the reactivity of the salts. Supplemental computations suggest the likely cation-interactions sites in the anions and provide a basis for designing more reactive charge-activated bases/nucleophiles with fewer "sparks" (i.e., less attraction) between the anions and cations.

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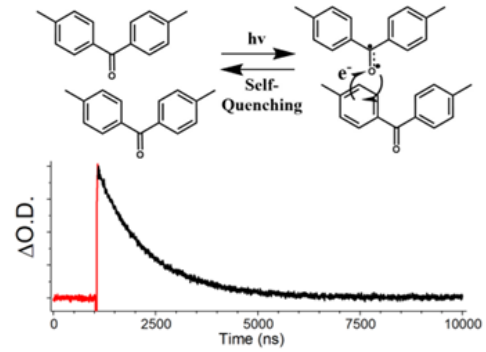
Kinetics of the Triplet Excited State of Photoreactive Nanocrystalline 4,4'-Dimethylbenzophenone: Relative Contributions from Intermolecular H-Atom Transfer and Self-Quenching

Jared King[1] and Miguel Garcia Garibay[1]

[1]*University of California, Los Angeles, USA*

Measuring the kinetics of photochemical reactions in crystals using conventional transmission spectroscopy methods has been challenging, primarily due to their high absorption and anisotropic optical properties. Recent work from our group has shown that aqueous nanocrystalline suspensions of molecular crystals with sizes smaller than the wavelength of light used for excitation (ca. 100-300 nm) are amenable for the use of transmission spectroscopy.[2]

Crystals of 4,4'-dimethylbenzophenone (DMBP) are known to react by intermolecular H-atom transfer followed by radical pair recombination. To determine the contribution of the H-atom transfer reaction for the deactivation of the triplet ketone, transient absorption spectra and kinetics were obtained using aqueous nanocrystalline suspensions. Single exponential triplet lifetimes of ca. 1185 ns with no deuterium isotope effect and inefficient product formation suggests that the reaction does not contribute significantly to the kinetics of triplet decay. By contrast, the observed lifetime is consistent with previous observations with p, p'-disubstituted benzophenones that undergo efficient self-quenching process by a reductive charge transfer mechanism.[2,3]



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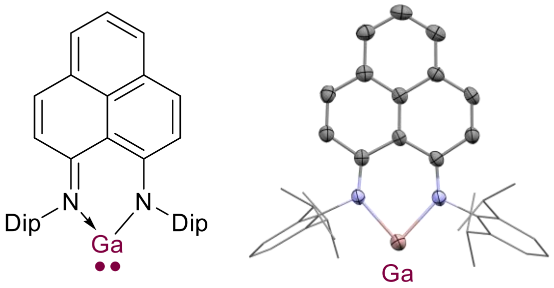
Synthesis, Structure, and Reactivity of Tetrylenes Bearing a Phenalenyl-Based Ligand

T. Kodama[1,2]

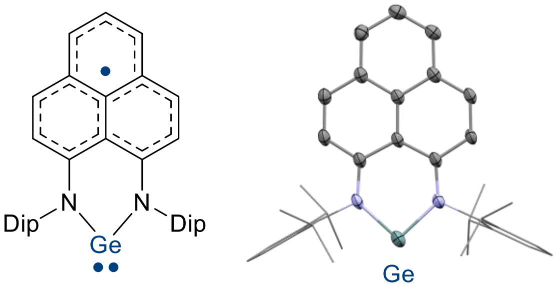
[1]*Graduate School of Engineering, Osaka University, Suita, Osaka, Japan*
[2] *ICS-OTRI, Osaka University, Suita, Osaka, Japan*

There has been a growing interest in tetrylenes and their analogs due to their distinctive structure, electronic properties, and reactivities. The key in the ongoing tetrylene chemistry is developing a rational ligand design to improve their stabilities and thus, development of new ligands is an important issue.

We recently synthesized and characterized gallylene **1** and open-shell germylene **2** stabilized by phenalenyl-based bidentate ligand. In solution, **1** has a high thermal stability at 80 °C, with an absorption maximum at 505 nm. Complex **1** promotes the oxidative addition of I–I, Si–Cl, C–I, and S–S bonds and oxidative cyclization with various π-components. Complex **1** can also coordinate to a tungsten complex to form a gallium–tungsten bond.[1] Complex **2** is possible to isolate compound **2** in crystalline form by sublimation at ca. 300 °C. ESR spectra, crystallographic analysis, theoretical calculations, and reactivities with carbon radicals suggest that the spin of **2** is distributed on the phenalenyl moiety, while **2** reacted with C_2Cl_6, PhSSPh, and *p*-benzoquinone at the germanium center to form Ge−E (E = Cl, S, O) bonds. Furthermore, compound **2** is featured by its reactivity as a “formal germylyne”, which allows for the formation of three new σ-bonds or one σ-bond with metal complexation on the germanium center.[2]



(DipN-PLY)Ga (**1**)



(DipN-PLY)Ge (**2**)

- oxidative addition of σ-bonds
- oxidative cyclization with π-components
- coordination to tungsten complex

- considerable thermal stability
- ambident radical reactivity
- reactivity as "formal germylyne"

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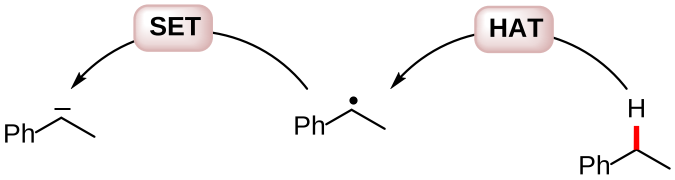
Generation of Carbanions by Light

B. König

Faculty of Chemistry and Pharmacy, University of Regensburg, Regensburg, Germany

The classic conversion of C-H bonds into carbanions relies on the use of strong bases, which, however, is inherently coupled with salt formation. An alternative approach uses hydrogen atom abstraction and subsequent reduction of the resulting carbon-centered radical.[1] We discuss the use of this photocatalytic method in organic synthesis[2,3,4] and details of the proposed mechanism.



Umpolung of carbonyl groups provides another useful access to carbanions.[5] We discuss photocatalytic carbonyl Umpolung reaction, their use in synthesis and mechanisms of action. [6,7]

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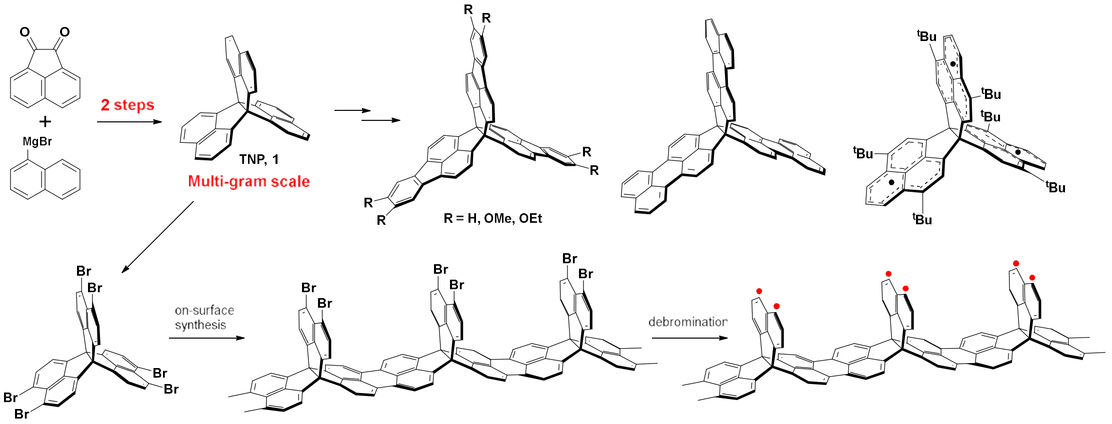
Recent studies on π-expanded trinaphtho[3.3.3]propellane

Takashi Kubo[1,2,3]

[1]Graduate School of Science, Osaka University, Toyonaka, Osaka, Japan
[2] Innovative Catalysis Science Division (ICS), Institute for Open and Transdisciplinary Research Initiatives (OTRI), Osaka University
[3] Spintronics Research Network Division, Institute for OTRI, Osaka University

Through-space interactions between cofacially aligned π-electron systems have played an important role in organic semiconductors such as organic field-effect transistors and photovoltaic devices. Compared with typical π-electron systems with a planar scaffold, in propeller-shaped π-electron systems such as triptycene, in which three aromatic rings are cofacially arranged at an angle of 120°, the three aromatic rings are able to interact with each other by spatial overlap of their molecular orbitals.

Recently, we have developed a new synthetic method that allows us to prepare trinaphtho[3.3.3]propellane (TNP, **1**) in two steps from commercially available compounds on a multi-gram scale [1]. We also π-expanded **1** to investigate the electronic interaction between π-blades and the stacking motif of molecules in solid state. In my lecture, our recent advances in the research of π-expanded TNPs will be discussed in detail [1–7].



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Reactive molecules investigated with *para*-hydrogen infrared matrix spectroscopy

Yuan-Pern Lee[1, 2]

[1] Department of Applied Chemistry and Institute of Molecular Science, National Yang Ming Chiao Tung University, Hsinchu 300093, Taiwan
[2] Center for Emergent Functional Matter Science, National Yang Ming Chiao Tung University, Hsinchu 300093, Taiwan

Solid *para*-hydrogen (p-H_2) matrix isolation has facilitated applications unachievable with noble-gas.[1] We took advantage of the diminished cage effect of p-H_2 to prepare C_6H_6Br from photolysis of $Br_2/C_6H_6/p$-H_2. The IR spectrum indicates that Br in C_6H_6Br migrates from one carbon atom to another, performing a bevel-gear-type rotation. This motion induces the stereo selectivity in the formation of *trans-ortho-* and *trans-para*-$C_6H_6Br_2$, eliminating the need of the formation of a cyclic (η_2)-C_6H_6Br radical proposed previously to explain the stereo selectivity. We performed electron bombardment on p-H_2 during deposition to produce H_3^+; H_3^+ readily transfers a proton to polycyclic aromatic hydrocarbons (PAH) to form protonated PAH, possible carriers of unidentified IR emission in astronomy. Some protonated species became neutralized to form mono-hydrogenated PAH. Examples include protonated and hydrogenated isoquinoline. We also utilized two novel methods to generate H atoms for reactions in darkness; H can efficiently tunnel through solid p-H_2 via H−H bond breaking and formation. One method is to add trace Cl_2 and photodissociate it at 365 nm to generate Cl atoms; subsequent IR irradiation activates $Cl + H_2$ ($v = 1$) $\rightarrow HCl + H$ to generate H atoms. Another method is to photolyze H_2O_2 near 250 nm to form OH, which reacts with H_2 to form $H_2O + H$; in darkness, this tunneling reaction can generate H atoms slowly and continuously, causing more significant H reactions. The experiment of H + methylamine using H_2O_2 showed that the H reaction proceeded much further as compared with that using Cl_2. In addition to the production of various isomers of hydrogenated species via H addition, such as H + PAH, we found that the H abstraction plays important roles. Examples include stepwise H abstraction from H + methylamine. These results introduce new concept in astrochemistry.[2] We also found that heavy atoms such as Cl can diffuse through solid p-H_2, enabling study of bimolecular reactions in solid p-H_2 and leading to a new concept of the quantum diffusion in solid p-H_2. The reaction kinetics of $Cl + C_2H_4$, $OH + C_2H_4$, $H + C_2H_4$ will be compared.

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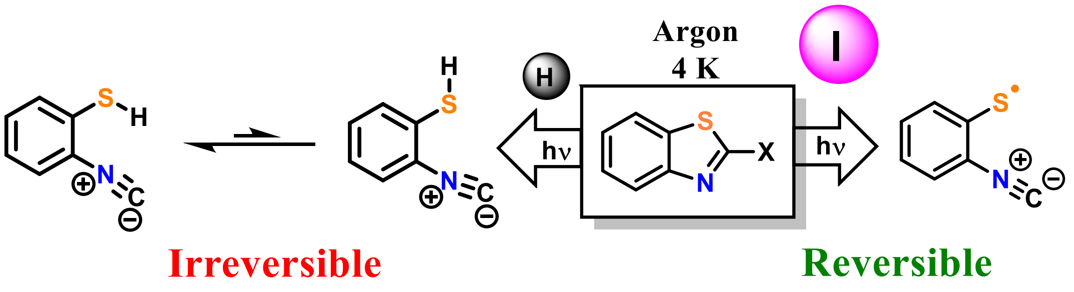
2-Isocyanophenylthiyl Radical and its Iodine-triggered Radical Cyclization in Solid Argon

Anjali Mahadevan[1], Piyush Kumar[1], Sapna Singh[1], and Sugumar Venkataramani*[1]

[1]Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER) Mohali, Sector 81, SAS Nagar, Knowledge City, Manauli, Punjab – 140306, INDIA.
Ph17017@iisermohali.ac.in.

Sulfur centered radical is one of the key reactive intermediates in several biomolecular processes and organic synthesis involving redox chemistry of disulfides and thiols.[1] Recently, Mardyukov and Schreiner reported the generation and reactivity of thiyl radical through flash vacuum pyrolysis (FVP) in cryogenic conditions.[2] Motivated by the challenges associated with the chemistry of thiyl radicals, we decided to investigate the photochemistry of 2- iodobenzothiazole (**IBT**) and benzothiazole (**BT**) in an argon matrix at 4 K. The benzene-fused **IBT** and **BT** as a precursor restricted the number of bond cleavages and limits the photoproducts. Interestingly, the UV irradiation of **IBT** led to the formation of 2-isocyanophenylthiyl radical **3**, which on subsequent 365 nm irradiation or annealing conditions reverted to the precursor **IBT** indicating an iodine-triggered thiyl radical-based cyclization. DFT computations were carried out in identifying the products and mechanistic aspects. Furthermore, control experiments using benzothiazole **BT** revealed the formation of 2- isocyanothiophenol without showing reversibility confirms the significance of C-I and C-S bonds in establishing the reversibility (**Scheme 1**)[3]



Scheme 1. Photochemistry of IBT and BT in solid argon at 4K

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Preparation and Exploration of Heavier Pnictogen Species

Artur Mardyukov, and Peter R. Schreiner
Justus Liebig University, Heinrich-Buff-Ring 17, 35392 Giessen

Emal: artur.mardyukov@org.chemie.uni-giessen.de

Owing to their roles as versatile reagents and pivotal intermediates in numerous chemical processes, the properties and reactivity of carbenes (R–C̈–R) and nitrenes (R–N̈:) have been extensively studied, despite their high reactivity.[1-2] However, there are still many families of reactive intermediates that have eluded isolation and spectroscopic identification. Among these are arsinidenes (R–Äs:), the neutral monovalent arsenic congeners of nitrenes, and phosphinidenes (R–P̈:) with six electrons in their valence shell. Multiple attempts have been made to prepare free arsinidenes, but the detection and identification of these species have been hampered by their instability and fleeting existence.[3] All other evidence for the existence of arsinidenes has been derived from trapping and complexation experiments. The talk reports the first synthesis, IR, and UV/Vis spectroscopic characterization of parent phenylarsinidene (**1**) and its reactions with small molecules (O_2, CO, NO) leading to several novel species that have not been reported (**2**-**5**) (Figure 1A).[4] We illustrate that the chemical transformations involved are distinctly different from those observed with triplet nitrenes[5] and phosphinidenes,[6-7] the lighter congeners of **1**.

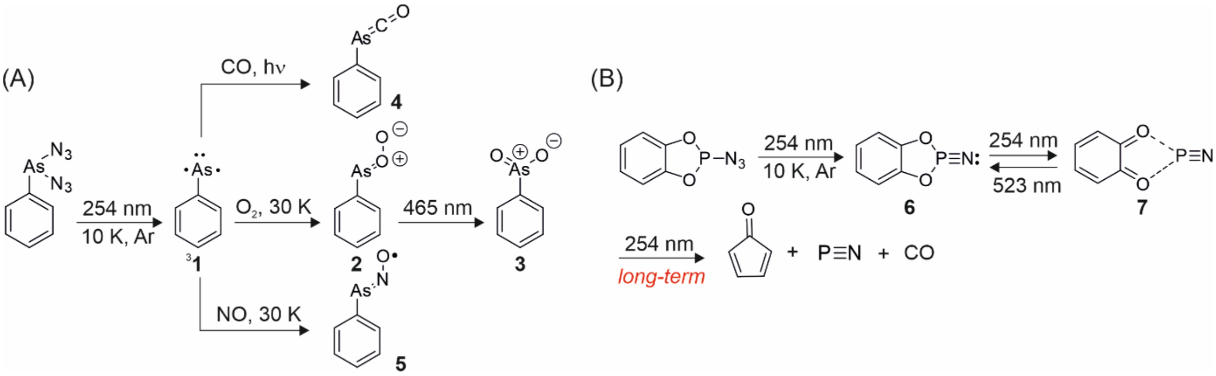

Figure 1. (A) Phenylarsinidene (**1**) and products of its reactions with O_2, CO, and NO. (B) Photochemical generation of **6** and **7** and subsequent reactivity.

The quest for molecular precursors that can release the extremely reactive heavier homologs of dinitrogen N_2, such as P_2, As_2, PN, is a fascinating area of research within the realm of group 15 element chemistry.[8-9] However, the high reactivity of PN and the absence of a suitable molecular precursor for its release have prompted scientists to synthesize molecules that contain embedded phosphorus monitride units.[9] Here we report the first PN-bearing van der Waals complex (**7**) that was generated in cryogenic matrices utilizing UV light irradiation of the corresponding azide precursor. Besides IR and UV spectroscopic characterization, its recombination to covalently bonded (o-phenyldioxyl)-λ_5-phosphinonitrile (**6**) was triggered by subsequent 523 nm irradiation through a concerted mechanism, which reveals the first observed reactivity of PN towards organic molecules (Figure 1B).[10]

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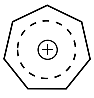
Taming Unstable Carbocations in Gas-Phase and Water Ice Matrices.

Enrique Mendez-Vega[1], **Patrick Hemberger**[2], **and Wolfram Sander**[1]

[1]Lehrstuhl für Organische Chemie II, Ruhr-Universität Bochum, 44780 Bochum, Germany
[2]Laboratory for Femtochemistry and Synchrotron Radiation, Paul Scherrer Institut, CH-5232 Villigen, Switzerland

Owing to their electron deficiency, carbocations are highly unstable, reactive, and short-lived under ambient conditions. Herein, we show that amorphous water ice is a suitable host to produce and kinetically stabilize unstable carbocations by protonation of carbenes. This reaction occurs via a hydrogen-bonded complex between the singlet carbene and a water molecule, while adjacent water molecules control the fate of the intermediates. Carbocations are also generated by UV–vis photo-induced electron detachment of the corresponding radicals, where water ice plays a key role by substantially lowering the ionization potential. Tropyl **1**, benzhydryl **2**, and the antiaromatic fluorenyl cation **3** have been isolated and characterized by IR and UV–vis spectroscopic in water ice matrices.[1-2] Micro- and macrosolvation, as well as thermal reactions of such elusive species can be monitored from 3 to 160 K.[3-4]

The pentafluorophenyl **4b** cation represents a greater challenge, due to its extreme electrophilicity and reactivity. This cation is alternatively produced in the gas phase via VUV photoionization of the radical and characterized by mass-selected threshold photoelectron spectroscopy (ms-TPES).[5] Vibrationally-resolved photoelectron spectra assisted by high-level ab-initio calculations, indicate that the cation is a $\pi^5\sigma^1$ diradical with nearly-degenerate open-shell singlet and triplet ground state, in stark contrast to the closed-shell singlet ($\pi^6\sigma^0$) phenyl cation **4a**.[6]



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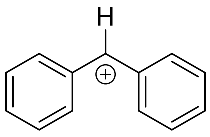

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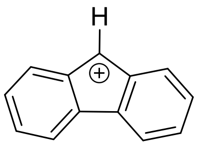

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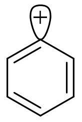
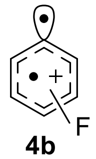


4a



4b

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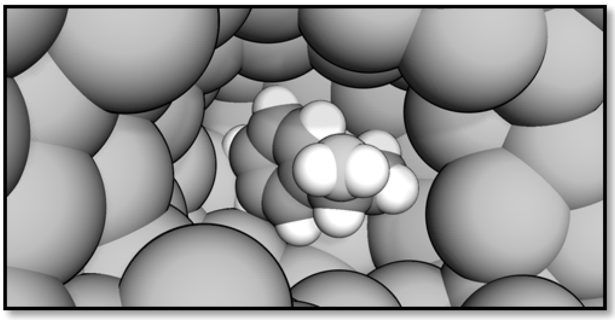
VCD spectroscopy under cryogenic conditions: Of matrix effects and photochemistry of chiral molecules

Christian Merten

Ruhr-Universität Bochum, Organische Chemie II, Bochum, Germany
christian.merten@ruhr-uni-bochum.de / www.mertenlab.de

Vibrational Circular Dichroism (VCD) spectroscopy measures the small difference in the absorption of left- and right circular polarized infrared light by a chiral sample. It allows the unambiguous assignment of absolute configurations by comparison of experimental and computationally predicted spectra,[1] but it is also highly sensitive to even very subtle differences in structures, such as conformational changes induced by solute-solvent interactions.[2] In our work, we take advantage of this conformational sensitivity and use VCD spectroscopy to probe intermolecular interactions of interest in catalysis[3] and supramolecular chemistry.



This talk will focus on our activities to combine VCD spectroscopy with the matrix-isolation technique. Highlighting some recent results, we show that trapping chiral molecules in solid rare gas matrices can help us understand problems faced in the interpretation of solution phase spectra. These challenges in the analysis are, for instance, flat potential energy surfaces[4] or chiral photoisomerization products.[5] As matrix effects were found to occasionally make the interpretation of MI-VCD spectra quite challenging, we also implemented an experimental setup to record VCD spectra in liquid rare gases. The first experiments using this cryosolutions-VCD setup helped us to reveal matrix-effects in MI-VCD spectra and to benchmark computational approaches for the prediction of anharmonic VCD intensities.[6,7]

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Porphene and Porphite: Porphyrin Analogs of Graphene and Graphite

Thomas F. Magnera[1], Paul I. Dron[1], Jared P. Bozzone[1], Milena Jovanoviæ[1], Igor Ronèeviæ[2],
Edward Tortorici[3], Wei Bu[4], Elisa M. Miller[5], Charles T. Rogers[3,6], and Josef Michl[1,2]

[1]Department of Chemistry, University of Colorado, Boulder, CO 80309, U.S.A.; [2]Institute of Organic Chemistry and Biochemistry, Czech Academy of Sciences; Prague, Czech Republic; [3]Department of Physics, University of Colorado, Boulder, Colorado 80309, U.S.A.; [4]ChemMatCARS, University of Chicago; Lemont, IL 60439, U.S.A.; [5]Chemistry and Nanoscience Center, National Renewable Energy Laboratory; Golden, CO 80401, U.S.A.; [6]Renewable and Sustainable Energy Institute (RASEI) at the University of Colorado, Boulder, CO 80303, U.S.A.

Two-dimensional materials have unusual properties and promise applications in nanoelectronics, spintronics, photonics, (electro)catalysis, separations, and elsewhere. Most are inorganic and their properties are difficult to tune. We have prepared Zn porphene, a member of a new organic metalloporphene family. Similar to graphene, these fully conjugated two-dimensional polymers are composed of fused metalloporphyrin rings. Zn porphene is synthesized on water surface by two-dimensional oxidative polymerization of a Langmuir bilayer of Zn porphyrin with K_2IrCl_6. It is transferable to other substrates and bridges ì m-sized pits. Contrary to previous theoretical predictions of metallic conductivity, it is a p-type semiconductor due to a Peierls distortion of its unit cell from square to rectangular, analogous to the appearance of bond-length alternation in antiaromatic molecules. Insertion of various metal ions, possibly carrying a fifth or sixth ligand, is reversible and promises tunability and patterning of circuits on an atomic canvas without removing any ð centers from conjugation.

Theoretical study of carbenes on metal surfaces

<u>Joel Mieres Perez</u>[1], Yunjun Cao[2], Karina Morgenstern[2], Wolfram Sander[3], and Elsa Sanchez-Garcia[1]

[1] Lehrstuhl für Computational Bioengineering, Technische Universität Dortmund, Dortmund, Germany
[2] Lehrstuhl Physikalische Chemie I, Ruhr-Universität Bochum, Bochum, Germany
[3] Lehrstuhl für Organische Chemie II, Ruhr-Universität Bochum, Bochum, Germany

We were able to characterize in real space a highly reactive carbene, fluorenylidene (FY) on Ag(111) in a combined theoretical and experimental study.[1] The FY carbene was generated by photolysis of a suitable precursor at low temperatures producing a metal-bound complex. Our simulations suggested that the depression observed in the STM images around the carbene center was due to a charge transfer between the surface and the carbene, in which the electron density is depleted from the surface and accumulated on the carbene. The strong interaction between the carbene and the surface, and the charge transfer from the surface to the carbene, drastically reduces the reactivity of the FY compared to that in solution. We also showed that the previous scenario changes completely if water is added to the surface before the carbene is generated. In this case, a new species is formed that draws electrons from the surfaces to a lesser extent than when water is not present.[2] The new species was assigned to the fluorenyl radical with a smaller adsorption energy compared to that of the carbene. In addition, a large species is formed due to the reaction of FY with water on Ag (111), which was assigned to the coupling product of the fluorenyl radical with the FY carbene or with diazofluorene. This final product resembles a radical species with different adsorption heights from both conjugated systems on opposite sides of the radical center. We are currently investigating the reactivity of different carbenes, e.g. diphenylcarbene (DPC), on metal surfaces. DPC shows an interesting reactivity on the surface, different from that of FY. These studies highlight the importance of controlling carbene reactivity by the combination of solvent interactions and absorption on metal surfaces.

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A local view on the influence of solvents on the reactivity of surface-catalyzed reactions

K. Morgenstern

[1]Physical Chemistry I, Ruhr-Universität Bochum, Germany
E-mail: karina.morgenstern@rub.de

A microscopic understanding of on-surface reactions involving highly reactive intermediates is challenging because a radical quickly loses its reactivity after its creation on a metallic surface via charge transfer whenever the reaction partner is not in the immediate vicinity. It is also true for carbenes, essential intermediates in multiple C–C bond forming processes such as cyclopropanations, insertion reactions, olefin metathesis. We explore in this talk how the solvent tunes the reactions pathways of carbene for two surface adsorbed carbene, diazofluorene on Ag(111) and diphenyl-carbene on Cu(111), that were investigated by low-temperature scanning tunneling microscopy and density functional calculation. Upon photolytic or thermal activation of their diazo-protected precursors, a charge transfer from the metal to the carbenes quenches their exceptional reactivity [1], leading to their anchoring to the surface via their reactive center [2]. To overcome this drawback for reactivity, we detach the N_2 group in the presence of water. The reaction condition alters the final product. Small amounts of water catalyze biflourene formation [3], while large ones result in the hydroxylation of carbene.

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A Plumba Triplet Carbene

A. Swain, J. Messelberger and D. Munz

Saarland University, Coordination Chemistry, Campus C4.1, Saarbrücken, Germany

Isolable triplet carbenes, albeit studied for decades, remain hitherto largely elusive except for sterically encumbered diaryl substitution patterns.[1] In this contribution, I will present on a formal plumba carbyne.[2] This exceedingly sensitive species is stable in solution up to -40°C,[3] yet may be isolated in the cold. Evans-NMR measurements in combination with quantum-chemical calculations indicate a triplet-carbene electronic structure without multiple bonding between the two-valent metal and the ligand. An *in-situ* SC-XRD study substantiates the swift *in-crystallo* activation of toluene even under cryogenic conditions.

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A Time-Resolved Look on Photochemical Processes for which Adjacent Molecules Play a Crucial Role

Patrick Nuernberger[1]

[1] *Institute of Physical and Theoretical Chemistry, University of Regensburg, Germany*

Three experiments are discussed in which the photodynamics of a molecule strongly depend on the environment, an effect that one can try to exploit in a desired fashion.

1,3,5-Triphenylformazan (TPF) is an important product for the enzymatic or light-induced reduction in tetrazolium assays, but its photodynamics are rather sensitive to external influences. Therefore, we investigated the behavior of TPF after excitation in different solvents on a broad time scale from femtoseconds up to minutes [1]. In combination with quantum-chemical calculations, we can assign how the various isomers are thermally and photochemically interconnected and conclude that proton transfer plays a decisive role during the isomerization pathway.

In a study on supramolecular hosts that can encapsulate small guest molecules, ultrafast spectroscopy was employed to address how the guest alters the photoswitching characteristics of the cage. For this, the impacts of three disparate guest compounds on ring-opening or ring-closure of a dithienylethene (DTE) ligand in a photoswitchable DTE-based coordination cage are juxtaposed. It is shown that the guest can modulate both the outcome and timescale of the cage's photodynamics [2].

Interaction with an adjacent molecule can also be employed for deracemization. The substrate binds to a chiral photocatalyst by two-point hydrogen bonding, i.e., a pre-complexation exists when the catalyst is excited by light. Two criteria have to be met for the reaction to work efficiently: First, light absorption triggers a transfer process that works better (or exclusively) for one of the enantiomers. Second, an achiral intermediate has to be formed whose lifetime exceeds that of the complex, so that the subsequent reformation of the chiral substrate is not enantioselective. For the deracemization of hydantoins [3], a hydrogen-atom transfer (HAT) to the chiral benzophenone catalyst occurs which is only possible for one hydantoin enantiomer due to steric reasons. The back HAT yields an achiral enol intermediate which reforms the hydantoin in a non-enantioselective way in an enol-keto tautomerization.

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Quantum tunneling reactions:
Discoveries on the Slippery PES of Arylnitrenes

Cláudio M. Nunes

University of Coimbra, CQC-IMS, Department of Chemistry,
3004-535 Coimbra, Portugal

Tunneling is a fascinating quantum mechanical phenomenon (QMT) that allows particles to permeate through potential energy barriers. QMT can manifest itself in ordinary reactions, and one obvious consequence is the increase of reaction rates compared to the expectation of the classical transition state theory (TST). A much more profound consequence of QMT is the control of chemical reaction outcomes, leading to new reactivity paradigms that break with the classic TST principles (e.g., the thermodynamic or kinetic reaction control).

Direct spectroscopic investigations at cryogenic temperatures have been decisive to shed light on the potential relevance of QMT in organic transformations and to reveal chemical reactivity beyond classical paradigms. In this communication, I will present our contributions to this research endeavor with highlight to our pioneering discoveries of QMT reactions on the slippery PES of arylnitrenes. These comprise: H-atom QMT [1] and H-atom QMT activated by precise IR radiation [2]; competitive heavy-atom QMT [3], and heavy-atom QMT through crossing surfaces [4]; and a remarkable case of simultaneous QMT control in conformer-specific reactions [5].

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Excited state aromaticity and antiaromaticity: From scopes to pitfalls

H. Ottosson[1]

[1]*Department of Chemistry – Ångström, Uppsala University, Uppsala, Sweden*

The use of excited state aromaticity and antiaromaticity (ESA & ESAA) to rationalize excited state properties and processes has grown rapidly in recent years.[1,2] There is a plethora of possible applications of the ESA & ESAA concepts, however, there are also limitations, complications and pitfalls. Excited state aromaticity is often taken as synonymous to Baird-aromaticity,[3] *i.e.*, aromaticity of $4n\pi$-electron cycles in their lowest π,π^* triplet states. Yet, instead of Baird-aromatic, some molecules are Hückel-aromatic or Hückel-Baird hybrid aromatic in their lowest excited states, while others are excited at different functional moieties than at the conjugated rings.[4-6] Singlet excited states are more numerous than the triplet states, and they are often more intricate computationally. States with different numbers of π_α- and π_β-electrons (*e.g.*, n,π^* states of some heteroaromatics) may also appear as aromatic according to computations.[7] Finally, there are differences between various computational methods and aromaticity descriptors. Thus, for the proper and efficient utilization of the ESA & ESAA concepts in various applications there are a number of fundamental aspects that need to be explored. In the talk I will give a brief overview of various complications, yet also show how the concepts can be of potential use in areas ranging from astrochemistry via organic photoreactivity and photophysics to design of new chromophores for tentative use in singlet fission photovoltaics.

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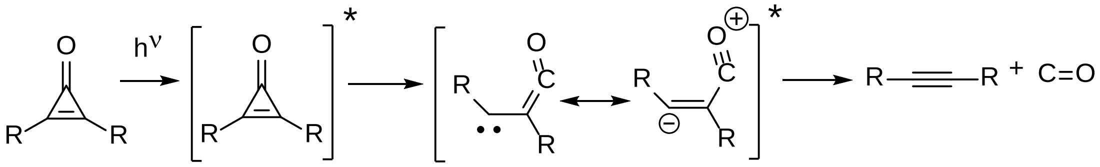
Media Effects on Photo-SPAAC Reaction

V. Popik

University of Georgia, Athens, GA, 30602, USA
E-mail: vpopik@uga.edu

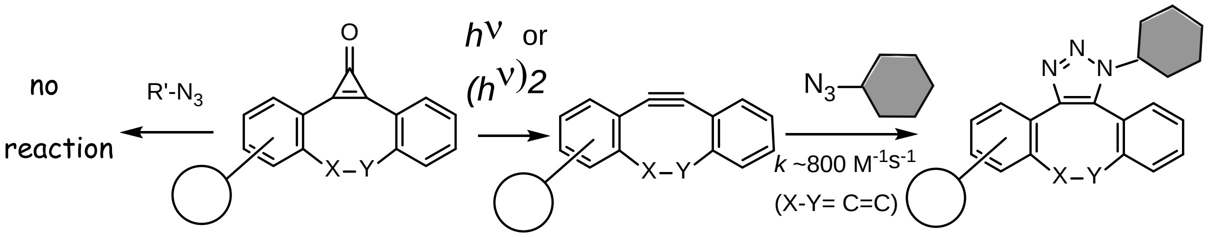
Photo-SPAAC (Strain Promoted Azide Alkyne Cycloaddition) ligation that has been recently developed in our laboratory relies on the photo-decarbonylation of cyclopropenone-caged dibenzocyclooctynes. Starting cyclopropenones do not react with organic or inorganic azides, nor with common nucleophiles or electrophiles and possess excellent thermal and hydrolytic stability. Irradiation with 350 – 420 nm light (or NIR pulses) converts them into azide-reactive cyclooctynes with high quantum efficiency (15 - 60%) and quantitative chemical yield.

The photo-decarbonylation proceeds via adiabatic sequential cleavage of C-C bonds. The lifetime of the excited state intermediate observed in this process is strongly affected by media.



τ = 39 ps (hexane); 168 ps (MeOH)

Photochemically generated dibenzocyclooctynes undergo quantitative SPAAC to organic azides with rates varying from 0.06 $M^{-1}s^{-1}$ to over 800 $M^{-1}s^{-1}$.



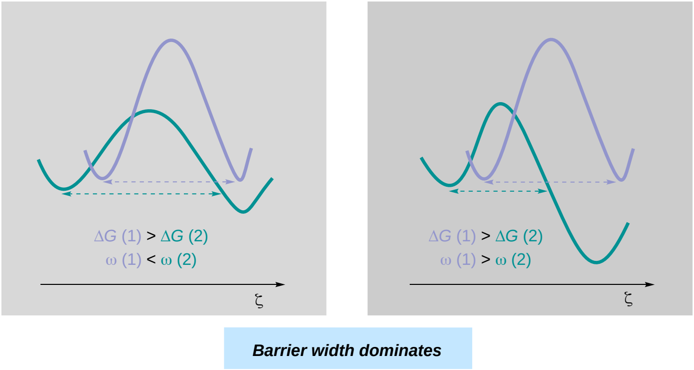
X-Y= CH_2-CH_2; C=C; CH_2-NR; CH_2-O

The actual rate of SPAAC depends not only on the structure of the reactants, but also on the medium. Thus, the most popular cyclooctyne in SPAAC ligation is ADIBO (AzaDIBenzocycloOctyne, a.k.a. DBCO and DIBAC), which we can generate from corresponding cyclopropenone (X-Y = CH_2-NR). It reacts with tetra-ethylene glycol azide (H-$(OCH_2CH_2)_4$-N_3) at 0.3 $M^{-1}s^{-1}$, 0.4 $M^{-1}s^{-1}$, and 2 $M^{-1}s^{-1}$ in THF, methanol, and water correspondingly. In organic solvent – water mixtures, the rate of SPAAC reaction grows exponentially with the increased water content. The solvent effects on the azide reactivity of several common cyclooctynes will be discussed.

The Intrinsic Barrier Width and its Role in Chemical Reactivity[1]

Peter R. Schreiner

Institute of Organic Chemistry, Justus Liebig University, Heinrich-Buff-Ring 17, 35392 Giessen, Germany



The Marcus dissection of the Gibbs activation energy (barrier height) into intrinsic and thermodynamic contributions,[2,3] which successfully models the interplay of rate and driving force, has led to a crucial general phenomenological consequence: the well-known two reactivity paradigms of “kinetic versus thermodynamic control”.[4] However, concepts analogous to the Marcus’ dissection for barrier *widths* are absent. Here we introduce the barrier-width-counterpart of the Marcus dissection: the concept of *intrinsic barrier width* and *driving force effect on the barrier width*, and report experimental as well as theoretical studies to demonstrate their distinct roles. We present the idea of changing the barrier widths of conformational isomerizations of some simple aromatic carboxylic acids[5] as models and use quantum mechanical tunneling (QMT) half-lives as a read-out for these changes.[6] This sheds light on resolving conflicting trends in chemical reactivities where barrier widths are relevant, and allows us to draw some important conclusions about the general relevance of barrier widths, their qualitative definition, and the consequences for more complete descriptions of chemical reactions based on one-dimensional reaction coordinates.

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Unlike Twins: H-Bonding in H_2S dimer, the “Big Brother” of Water Dimer

S. Jäger[1], J. Khatri[1], S.Henkel[1], P. Meyer[1], G. Schwaab[1] and M. Havenith[1]

[1] *Physical Chemistry 2, Ruhr University Bochum, Bochum, Germany*

While water dimer is intensively discussed in the literature,[1,2] its “Big Brother”, H_2S dimer received less interest from experimentalists.[3] The intermolecular interaction is expected to be weaker and the electrostatic interaction less directional than in case of water dimer. Here, we report high resolution IR spectra of the H_2S dimer in superfluid helium nanodroplets in the frequency range of the bound S-H stretch. We resolve a tunneling-rotational substructure, which allows a sensitive test of the potential energy surface. Based on the experimentally observed intensity alternation between subsequent rotational levels we can unambiguously assign these transitions to vibrational-rotational-tunneling (VRT) spectra of H_2S dimer (para-para, ortho-para, ortho-ortho) from the ground state to the vibrationally excited bound S-H stretch. By comparison with high level predictions of the energy splittings in the ground state we could deduce the tunneling splittings in the vibrationally excited state. We discuss the nature of the tunneling processes and the large amplitude intermolecular vibrations in comparison to water dimer.

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The Role of the Solvent in Turning Photodissociation into Photoisomerization and in Quantum Decoherence

William R. Borrelli,[1] Kenneth J. Mei,[1] Andy Vong,[1]
Devon R. Widmer,[1] and Benjamin J. Schwartz[1]

[1] Dept. Chem. & Biochem., UCLA, Los Angeles, CA, USA
E-mail: schwartz@chem.ucla.edu

For simple solution-phase chemical reactions, such as the photodissociation of a diatomic molecule, is it appropriate to assume that the potentials energy surfaces of the molecule are the same in solution as in the gas phase? If not, what modifications need to be made because of the solute-solvent interactions? In this talk, we explore what happens where there are relatively modest local specific interactions between a solute and solvent, with strengths on the order of that of an H-bond. By performing quantum simulations of the Na_2 and Na_2^+ molecules in a variety of liquids, we find that the solvent not only controls the bond dynamics of the solute, but that the solvent actually becomes part of the chemical identity of the solute.[1] For different coordination states of the solute by the solvent, there are entirely different bond lengths, vibrational spectra and electronic structure.[2] We show that once in the solvent, photoexcitation of Na_2^+ actually leads to a photoisomerization reaction rather than photodissociation, as in the gas phase.[3] We also show the chemical identity of the solute can change during the reaction and that linear response can fail, exemplifying the complexity of chemical reactivity in solution.[4] Finally, we explore how the solvent induces quantum decoherence during bond-breaking, determining the products of the chemical reaction.[5]

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Dynamic Effects on Selectivity of Organic Reactions in Solvent

Dean J. Tantillo

Department of Chemistry, University of California – Davis, Davis, CA, 95616, USA

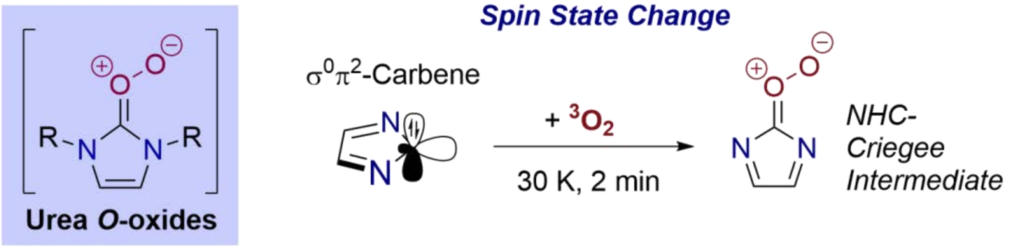
Ab initio direct dynamics simulations of organic reactions in solvent will be described with a focus on non-statistical dynamic effects that influence the selectivity of these reactions. Connections between the effects of solvents and microenvironments of catalyst active sites will be discussed. Electrostatic effects, preorganization, and cage effects will be highlighted using examples from the areas of organic synthesis, organometallic chemistry, and natural products biosynthesis.

Urea-*O*-Oxides: Criegee Intermediates from N-heterocyclic Carbenes

J. Philipp Wagner[1] and S. Medvedko[1,2]

[1]Institut für Organische Chemie, Eberhard Karls Universität Tübingen, Auf der Morgenstelle 18, 72076 Tübingen, Germany
[2] Department of Organic Chemistry, National Technical University of Ukraine "Igor Sikorsky Kyiv Polytechnic Institute", Peremohy Ave. 37, 03056 Kyiv, Ukraine

Carbonyl-*O*-oxides, commonly known as Criegee intermediates, are the central reactive species in the ozonolysis of alkenes.[1] Alternatively, they can be prepared from triplet carbenes and triplet molecular oxygen in an overall spin-conserving addition reaction.[2] However, singlet carbenes exhibit a rather sluggish reactivity towards O_2 leaving the corresponding carbonyl oxides largely uncharacterized, in particular those derived from N-heterocyclic carbenes (NHC).[3] In order to circumvent this problem, we have studied the reactivity of the highly electrophilic singlet NHC 2*H*-imidazol-2-ylidene, which exhibits its lone-pair in a π-orbital leaving the σ-orbital vacant.[4] This singlet carbene adds triplet O_2 at temperatures as low as 30 K under formation of a carbonyl oxide despite the need for a spin-state change.[5] In another approach, we have studied the reaction paths of N-heterocyclic olefin ozonolysis and found that these reactions do not result in the formation of Criegee intermediates but produce single oxygen atom transfer products instead which can be viewed as carbonyl-carbene adducts.



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Mapping fundamental chemical processes in gas & liquid using MeV electrons

X.J. Wang

SLAC National Accelerator Laboratory, Menlo Park, USA

Mapping fundamental chemical processes, such as the atomic-scale structural dynamics of molecules, visualizing chemical reactions, transformations, and the making and breaking of chemical bonds, are critical for understanding and control chemical reactions. X-ray Free Electron Laser (XFEL) is a revolutionary tool mapping fundamental chemical process; and MeV electrons is now also being explored for mapping fundamental chemical processes in gas & liquid [1-3]. MeV ultrafast electron scattering became a new frontier in ultrafast science due to its capability of following dynamics on femtoseconds scale with the high spatial resolution and sensitivity [4-5]. MeV ultrafast electron diffraction (MeV-UED) had broad and transformative impact on ultrafast science, such as light-induced transient states of quantum materials [6-7], the first direct imaging of fundamental chemical processes in gas [8-9] and hydrogen bond dynamics in liquid water [10]. MeV-UED is uniquely positioned to track reactive molecules during solvation process because its sensitivity to hydrogen and large momentum transfer. Large momentum transfer not only improves structure information, but also provides better separation between solute and solvent contributions [11].

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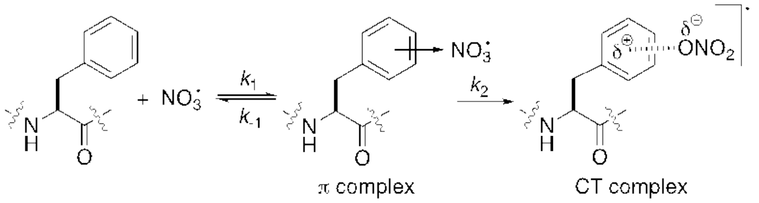
Phenylalanine Residues are Very Rapidly Damaged by $NO_3^\bullet$ in an Aqueous Environment

J. G. Nathanael and U. Wille

School of Chemistry, The University of Melbourne, Parkville, VIC 3010, Australia

Air pollution is a leading risk factor for global mortality, being responsible for about seven million premature deaths per year Particularly, inhalation of the toxic gases nitrogen dioxide ($NO_2^\bullet$) and ozone (O_3) can cause oxidative stress in biological systems. In healthy organisms, small-molecule antioxidants that deactivate the oxidants (or their precursors), and enzymes that repair already damaged biomolecules, act as a defence shield in the airway surface fluids (ASF) of the respiratory tract and lungs. Prolonged exposure to oxidizing air pollutants can lead to a breakdown of this defence mechanism, causing direct damage to proteins and lipids on cell surfaces or in the ASF. The resulting highly reactive protein and lipid oxidation products could harm epithelial cells in subsequent steps, which could result in inflammation.

In our effort to understand the mechanism of oxidative damage in biomolecules exposed to $NO_2^\bullet$ and O_3 (for example, upon inhalation) we have performed kinetic studies, which revealed that nitrate radicals ($NO_3^\bullet$), which are formed through reaction of $NO_2^\bullet$ and O_3, very rapidly oxidize phenylalanine (Phe) residues in an aqueous environment, with overall rate coefficients in the 10^8-10^9 M^{-1} s^{-1} range.[1] Using amino acids and dipeptides as model systems, the data suggest that the reaction proceeds via a π-complex between $NO_3^\bullet$ and the aromatic ring in Phe, which subsequently decays into a charge transfer (CT) complex.



The stability of the π-complex is sequence-dependent and is increased when Phe is at the N-terminus of the dipeptide. Computations revealed that the considerably more rapid radical-induced oxidation of Phe residues in both neutral and acidic aqueous environments, compared to acetonitrile, can be attributed to the stabilization of the CT complex by the protic solvent, clearly highlighting the health-damaging potential of exposure to combined $NO_2^\bullet$ and O_3.

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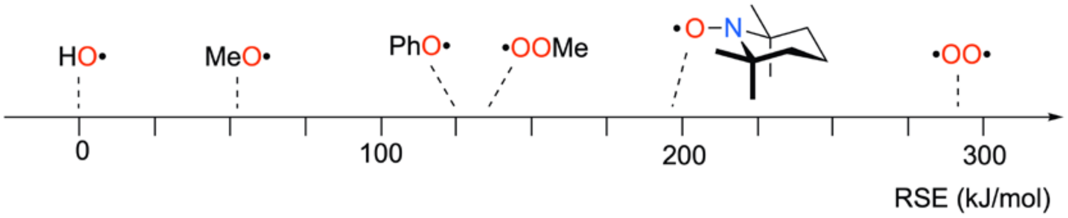
The Stability of O-Centered Radicals

H. Zipse

Dept. Chemistry, LMU München, München, Germany

O-Centered radicals are involved as transient intermediates in reactions as diverse as the oxidation of C5-modified nucleotide bases in the context of epigenetic regulation or the redox-mediated coupling of peptides with polyphenols.[1,2] Their stability values are, in combination with C-H bond energies, instrumental for the development of coherent mechanistic schemes.



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Abstracts of Posters

(in alphabetical order)

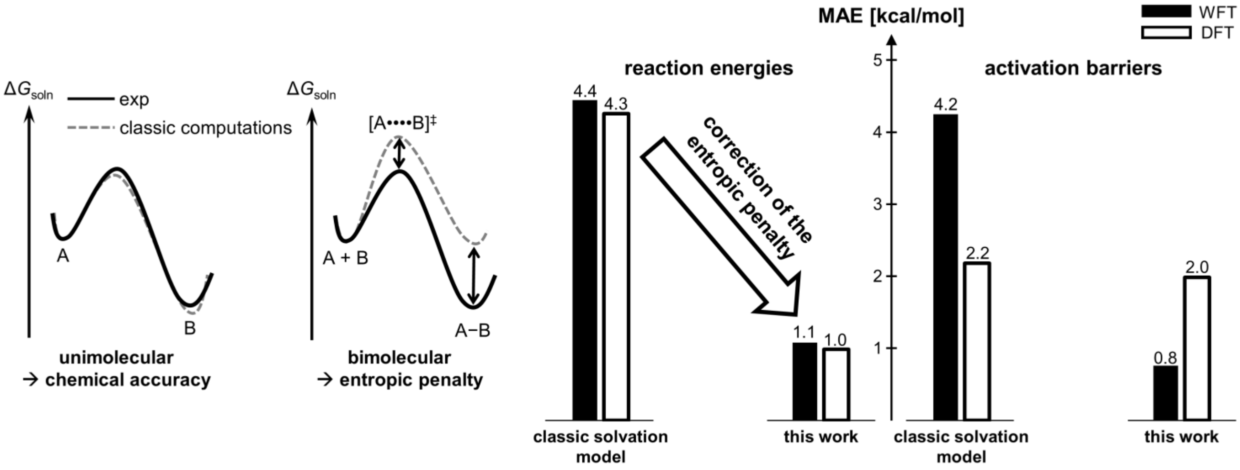
The Entropic Penalty for Associative Reactions and their Physical Treatment during Routine Computations

Jama Ariai[1], Urs Gellrich[1]

[1] *Institute of Organic Chemistry, Justus Liebig University, Heinrich-Buff-Ring 17, 35392 Giessen, Germany.*

In common praxis, solution-phase free energies G_{soln} are calculated by summing up the gas-phase free energies G_{g} (from QM computations) and solvation free energies $\Delta_{\mathrm{solv}}G$. The latter are derived from additional computations using continuum solvation models. However, due to their fitting parameters, entropy effects resulting from a change in molecularity are not correctly accounted for by these models. Therefore, entropy changes in bimolecular reactions in solution, e.g., S_N2 reactions and dimerizations, are overestimated and are penalized.

We studied this entropic penalty systematically for associative reactions in solution.[1] Indeed, typical computational protocols employing implicit solvent models overestimate ΔG_{soln} by 2−11 kcal/mol. We proposed an additive correction scheme based on Garza's formalism of the solution-phase entropy that is physically sound and easily implementable without an additional QM computation.[2] To validate our approach, we compiled an experimental benchmark set (31 Gibbs free reaction energies $\Delta_{\mathrm{r}}G_{\mathrm{soln}}$, 22 Gibbs free reaction barriers $\Delta^{\ddagger}G_{\mathrm{soln}}$ in 15 solvents) and considered representative best-practice protocols at the wavefunction theory (WFT) and density functional theory (DFT) levels. The corrected $\Delta_{\mathrm{r}}G_{\mathrm{soln}}$ achieved chemical accuracy (deviation <1 kcal/mol), and the same applies for $\Delta^{\ddagger}G_{\mathrm{soln}}$ at the WFT level. Barriers at the DFT level were slightly underestimated (2 kcal/mol) after the correction.



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Nitrenes and Chirality in Cryogenic Matrices

F. Beyer[1] and C. Merten[1]

[1]Ruhr-Universität Bochum, Bochum, Germany

Employing the matrix isolation (MI) technique, we characterized enantiopure 2-azidofluoren-9-ol by Infrared (IR) and Vibrational Circular Dichroism (VCD) spectroscopy as a precursor to the chiral triplet nitrene 2-nitrenofluoren-9-ol.

While MI-IR spectroscopy is well-established,[1] MI-VCD spectroscopy[2] is less commonly employed but a valuable tool to investigate e.g. weak intermolecular interactions[3] or chirality transfer as it is much more sensitive to conformational changes than the parent IR. However, VCD spectroscopy struggles with intrinsically low signal intensities; therefore, a good optical quality of the matrix is essential and sometimes challenging. Our experiments aim for an amplification of the VCD signal intensity by generating high spin structures which have an increased magnetic transition dipole moment (MTDM).

Until now, an enantiomeric resolution of the precursor 2-azidofluoren-9-ol was achieved and its VCD solution spectra were recorded. Furthermore, the photolysis of the precursor was studied by IR spectroscopy in argon at 20 K and showed the generation of triplet nitrene upon irradiation of the matrix at 254 nm.

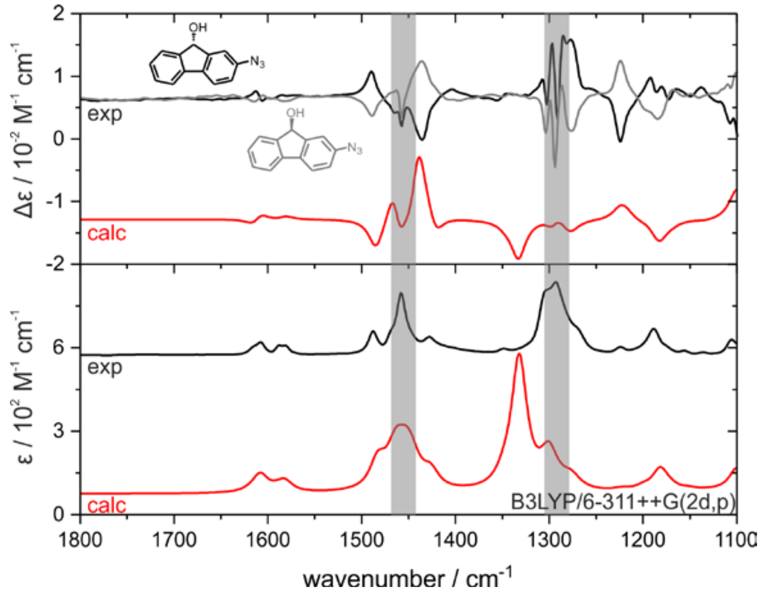

Figure 1: Experimental IR (bottom, black) and VCD (top, black) solution spectra of 2-azidofluoren-9-ol in DMSO-d_6 in comparison to calculated spectra (red) at B3LYP/6-311++G(2d,p) level of theory.

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Infrared spectra of isomers of protonated and hydrogenated phenanthrene isolated in solid *para*-hydrogen

J.-Y. Feng[1] **and Y.-P. Lee**[1,2]

[1] *Department of Applied Chemistry and Institute of Molecular Science, National Yang Ming Chiao Tung University, 1001, Ta-Hsueh Road, Hsinchu 300093, Taiwan*
[2] *Center for Emergent Functional Matter Science, National Yang Ming Chiao Tung University, 1001, Ta-Hsueh Road, Hsinchu 300093, Taiwan*

In this work, we focused on the vibrational absorption spectra of protonated and hydrogenated phenanthrene ($C_{14}H_{10}$) isolated in solid *para*-hydrogen (*p*-H_2). *p*-H_2 flowed through and mixed with phenanthrene vapor before deposition onto the nickel-plated Cu substrate at 3.2 K. During deposition, we used an electron gun to bombard the mixture of *p*-H_2 and $C_{14}H_{10}$ to generate $H^+C_{14}H_{10}$ and $HC_{14}H_{10}$. Electron bombardment of H_2 produced H_3^+ and H; the former can readily transfer its proton to $C_{14}H_{10}$ to form $H^+C_{14}H_{10}$, whereas the reaction of the latter with $C_{14}H_{10}$ and neutralization of $H^+C_{14}H_{10}$ generated $HC_{14}H_{10}$. Protonated species are expected to decrease in darkness over time through the neutralization process with trapped electrons to produce hydrogenated species. By observing the decay and the increase of infrared absorption lines, we could unambiguously classify features associated with protonated or hydrogenated species after the matrix was maintained in darkness for an extended period. $C_{14}H_{10}$ has a total of seven protonation or hydrogenation sites, including two for the carbons on the fused ring. Among isomers of $H^+C_{14}H_{10}$ or $HC_{14}H_{10}$, spectral assignments were achieved according to the behaviour upon secondary irradiation and a comparison of experimental results with vibrational wavenumbers and IR intensities predicted with the B3LYP/6-311++G(d,p) method. For $H^+C_{14}H_{10}$, secondary irradiation was performed at 619, 544, 524, and 463 nm. The absorption lines of $H^+C_{14}H_{10}$ could be divided into 4 groups and assigned to 10-, 1-, 3-, and 4-$H^+C_{14}H_{10}$, respectively. In the case of $HC_{14}H_{10}$, secondary irradiation at 423, 380, 315, and 223 nm helped to identify 1-, 4-, 3-, 10-, and 2-$HC_{14}H_{10}$; only hydrogenation at the carbon on the fused ring was not observed. Nearly all feasible protonated and hydrogenated PAH were produced and identified in one experiment; all spectra are new.

References

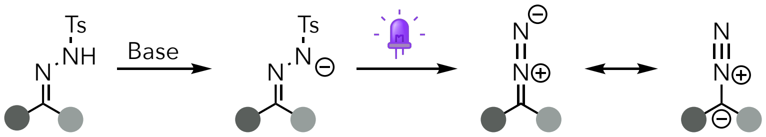
Photogenerated donor-donor diazo compounds enable facile access to spirocyclopropanes

Vincent George[1] **and Burkhard König**[1*]

[1]*Faculty of Chemistry and Pharmacy, University of Regensburg,*
Universitätsstraße 31 93040 Regensburg, Germany

Diazo compounds are well-known ambiphilic and versatile reagents in organic synthesis. Although they can serve as electrophiles, carbene precursors, or nucleophiles, there are very few reports for the latter. The main reason for this is the unstable and hazardous nature of the diazo moiety when not stabilized by adjacent groups. Therefore, most applications rely on bench-stable acceptor-acceptor or donor-acceptor systems.[1] This not only limits their reactivity, as the electron density of the reactive center decreases sharply, but also the range of substrates. Thus, easy access to donor-donor diazo compounds could not only expand the known reaction catalog, but also improve existing reactions with higher reactivity and fewer substrate limitations.

We have recently shown that in situ deprotonation and excitation of tosylhydrazones can lead to the formation of highly reactive donor-donor diazo compounds mitigating the risks associated with handling the active species directly (see Scheme 1).[2] With this new system in hand, we can envision its application in a variety of classical and novel reactions to effectively utilize the electronic structure. Further on, the focus shifted towards 1,3-dipolar cycloadditions for the synthesis of heterocycles and cyclopropanes to synthesize complex systems from simple starting materials opening a wealth of possible applications for synthesis and bioactive compounds.[3]



Scheme 1. Principle of the photoinduced in situ generation of donor-donor diazo compounds from tosylhydrazones.

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Hydrogen bonding and tunnling in $H_2O\cdots H_2S$ clusters

Stefan Henkel, Philipp Meyer, Svenja Jäger, Jai Khatri,
Gerhard Schwaab and Martina Havenith*
Lehrstuhl für Physikalische Chemie II, Ruhr-Universität Bochum, Germany.

We have studied the IR spectrum of H_2S and H_2O in helium nanodroplets at 0.37 K by laser spectroscopy. We have found only one isomer ($HOH\cdots SH_2$), for which we probe the bound and unbound OD stretching vibrations of $DOD\cdots SH_2$, $D^{18}OD\cdots SH_2$ and $DOD\cdots SD_2$. The bound OD stretching vibration is divided into four signals with one very large splitting (>30 cm^{-1}), and the signals can be assigned to vibrational rotational tunneling (VRT) transitions. Some of these bands show a rotationally resolved structure. All bands were assigned to parallel transitions ($K = 0 \leftarrow 0$) from the four VRT levels of A_1, B_1, B_2 and A_2 symmetry. This is in line with earlier microwave studies.[1] For the unbound OD stretch only two signals were observed.

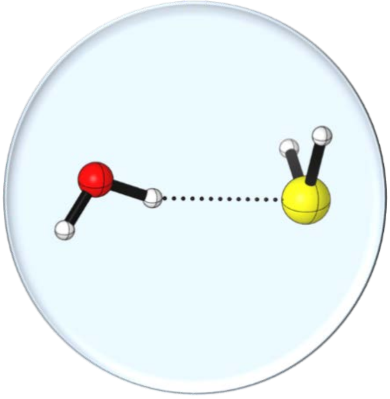

Fig. 1: Calculated $HOH\cdots SH_2$ hydrogen bond (B3LYP-D3/6-311+G(d,p)).

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SOMO-HOMO conversion of radical species within the CPP structure

K. Kajikawa, A. Itasaka, R. Murata, and M. Abe

Hiroshima University, Higashihiroshima, Hiroshima, Japan.

SOMO-HOMO conversion (SHC) is a phenomenon in which the SOMO and HOMO energy levels are inverted. Normally, the SOMO is arranged at a higher energy level than the HOMO in radical species. However, there are radical species in which the SOMO is in a lower energy level than the HOMO.[1-2] Here, we report molecules incorporating radicals such as nitroxyl radical and carbene within cycloparaphenylene (CPP) structures, which show SHC.[3] In addition, we report the generation and characterization of carbenes embedded in CPP.

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Generation, Photoionization, and Reactivity of Phenylethynyl Radical – Insights into Interstellar Chemistry

Ginny Karir[1], **Enrique Mendez-Vega**[1], **Adrian Portela-Gonzalez**[1], **Mayank Saraswat**[1], **Patrick Hemberger**[2], and **Wolfram Sander**[1]

[1]*Lehrstuhl für Organische Chemie II, Ruhr-Universität Bochum, 44780 Bochum, Germany*

[2]*Laboratory for Femtochemistry and Synchrotron Radiation, Paul Scherrer Institut, CH-5232 Villigen, Switzerland*

In this work, we report the gas-phase generation of the extremely reactive phenylethynyl radical (C_6H_5-CC•) and its reaction with acetylene, using mass spectrometry (MS) and photoion threshold photoelectron spectroscopy (TPES).Flash vacuum pyrolysis (FVP) of the precursors phenylethynyl iodide C_6H_5CC–I and phenylethynyl bromide C_6H_5CC–Br seeded in He were used to generate the highly reactive phenylethynyl radical (C_6H_5-CC•) in the temperature range of 1000–1600 °C. However only traces of this elusive radical (m/z 101) were detected by means of mass spectrometry, instead, the H-abstraction product, phenylacetylene C_6H_5CC–H (m/z 102), was formed in high yields. Pyrolysis at higher temperatures resulted in formation of m/z 100 (C_8H_4) by loss of hydrogen atom from phenylethynyl radical. The potential energy surface of C_8H_4 was explored to identify the thermally formed isomers. The fitting of Frank-Condon simulations of all possible isomers with the experimental TPE spectra confirms the presence of substituted benzynes as well as open chain polyynes. We also investigated the reaction of neat acetylene with the elusive phenylethynyl radical in the gas phase. The reaction results in the formation of an addition product at m/z 126 which can be conferred to a mixture of polyaromatic hydrocarbons (PAHs) with formulae ($C_{10}H_6$).

Photochemistry of 2-Iodoimidazole: A Computational and Matrix Isolation Infrared Spectroscopic studies.

Piyush Kumar[1], **Anjali Mahadevan**[1], **and Sugumar Venkataramani***[1]

Department of Chemical Sciences, Indian Institute of Science Education and Research (IISER) Mohali, Sector 81, SAS Nagar, Knowledge City, Manauli, Punjab – 140306, India.

N-Heterocycles and their associated radicals play a significant role in the interstellar medium (ISM).[1] Recent studies have also shown that they can be generated from the relatively simpler and prototypical precursors such as NH_3(ammonia), NH_2CHO(formamide) etc. that are known to exist in ice grains.[2] From the biogenesis perspective, the generation of imidazole, indole, and pyrrolidine, which are residues of histidine, tryptophan, and proline respectively, would be particularly intriguing.[3] Besides that, the intermediacy of radical species are equally important in the generation of heterocycles. In this regard, we have considered the five membered nitrogen-rich heterocycle-based 2-iodoimidazole as the precursor molecule to generate imidazole radical. To the best of our knowledge matrix isolation studies under cryogenic conditions has not been carried out on 2-iodoimidazole. After isolation of the 2-iodoimidaole (**2-IM**) in an argon and nitrogen matrix, photochemical studies were carried out at 4K. The introduction of a photo-labile iodine atom (I) facilitates the formation of a *C*-centered 2-dehydroimidazole radical. Further irradiation led to photo-fragmented products, realized from the characteristic IR frequencies corresponding to -CN and -NC groups. The preliminary results of the photochemistry of the 2-iodoimidazole under matrix isolation condition in combination with Density Functional Theory (DFT) computations will be presented through this contribution.

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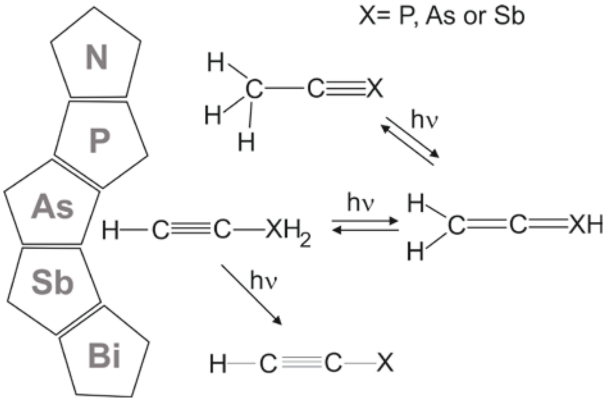
Free ethynylpnictinidenes: Matrix isolation and spectroscopic studies

A-L. Lawzer[1], E. Ganesan[1], T. Custer[1], M. Gronowski[1], J-C. Guillemin[2] and R. Kołos[1]

[1]*Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland*
[2] *University of Rennes, Ecole Nationale Supérieure de Chimie de Rennes, France*

Pnictogens are elements in group 15 of the periodic table and include N, P, As, Sb, and Bi. Pnictinidenes are neutral molecules with a univalent pnictogen atom containing a sextet of valence electrons. They generally have a triplet electronic ground state and are highly reactive. Nitrenes are the most familiar members of the pnictinidene family. In the past decade, several free phosphinidenes and a few heavier pnictinidenes have been characterized.

We have photochemically generate ethynylpnictinidenes (HCCX, X=P, As and Sb) in an argon matrix through direct photodehydrogenation of ethynylpnictines ($HCCXH_2$, X=P, As, Sb).[1] The ethynylpnictines can undergo dehydrogenation and tautomerization photochemically. The tautomerization process competes equally with dehydrogenation in ethynylphosphine whereas in ethynylarsine and ethynylstibine, it is unobservable.



Comparison of the electronic structures of HCCX (X=N, P, As or Sb) molecules indicates that the univalent character of a pnictogen atom is better pronounced in HCCAs and HCCSb than in HCCP, with HCCN being an exception as cyanocarbene. The vibrational and electronic absorption spectra of these species support this as well.

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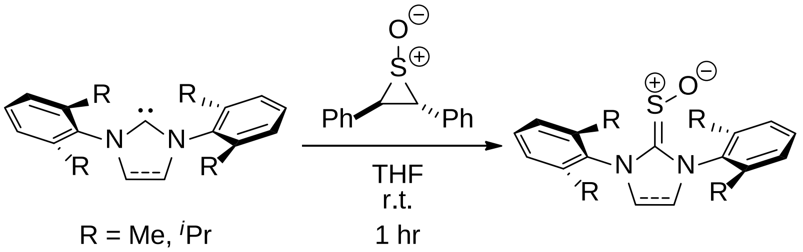
Synthesis of Thiourea S-Oxides *via* Formal SO Transfer from Thiirane Oxides

S. Medvedko[1,2] and J.P. Wagner[1]

[1] Eberhard Karls Universität Tübingen, Tübingen, Germany
[2] Igor Sikorsky Kyiv Polytechnic Institute, Kyiv, Ukraine
E-mail: philipp.wagner@orgchem.uni-tuebingen.de



Thiourea *S*-oxides can be considered as more stable heavier homologues of the currently unknown amino-substituted Criegee intermediates. [1] The latter have been suggested to enjoy significant resonance stabilization, but remain elusive to this day. [2,3] A subclass of the former, namely, imidazolidine-based thiourea *S*-oxides, was recently made synthetically available through direct thiourea oxidation by our group. [4] However, the limited applicability and moderate yield of this reaction prompted us to explore alternative methods based on the formal transfer of an SO molecule onto N-heterocyclic carbenes (NHCs).

The thermal decomposition of thiirane oxides has long been known to release the highly reactive sulfur monoxide triplet diradical, which can in turn be trapped by suitable scavengers. [5] While free SO might be expected to show limited reactivity towards NHCs due to the necessary spin-state change, [6] we have surprisingly discovered that the reaction between NHCs and *trans*-stilbene episulfoxide takes place at room temperature and forms the desired sulfines in good yields. The conditions of the procedure indicate that the mechanism of sulfur monoxide transfer here does not involve fragmentation of the thiirane oxide, but rather a nucleophilic substitution at a sulfur center. Hence, thiirane oxides constitute a convenient source of SO for the desired reaction that is more easily available than previously employed reagents. [7] Furthermore, our findings suggest that the scope of substrates can be greatly expanded by various singlet carbenes and other reactive nucleophiles.

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Exploring Photoreactivity and Photodynamic Behavior of (1-azidoethene-1,2-diyl)dibenzene and 2,3-Diphenyl-2H-azirine

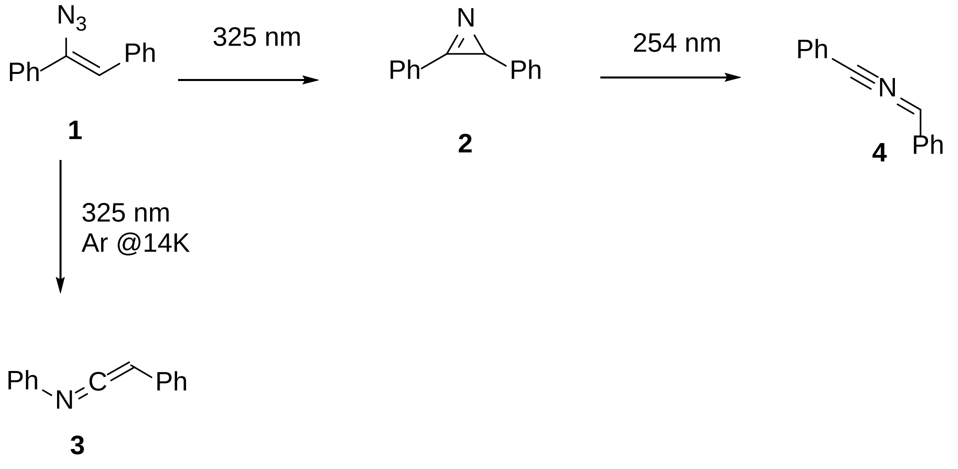
W. Dinindu Mendis, Katrin Vilinsky, Katrina A. Sumarli, Wandana H. Mohottige, Janaka Kavikarage,
Jeanette A. Krause, Bruce Ault, Anna Gudmundsdottir*

†Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221-0172, United States

Smart materials respond to external stimuli such as light, moisture, heat, and electric or magnetic fields, and are used in numerous applications including robotics, sensors, and actuators in industrial processes. Organic crystals have the ability to change light energy into mechanical work by twisting, coiling, crawling, bending, fracturing, or shattering.[1]

Herein we report on the photoreactivity and photodynamic behavior of (1-azidoethene-1,2-diyl)dibenzene **1** and 2,3-diphenyl-2H-azirine **2**. We studied the photochemistry of stilbene azide **1** in solution and cryogenic matrices as a function of irradiation wavelength. Irradiation of **1** with 325 nm at cryogenic argon matrices results in formation of azirine **2** and ketenimine **3**. In contrast, irradiation of **1** with 254 nm light in argon matrices resulted in formation of ylide **4** and more of ketenimine **3**. Furthermore, azirine **2** reacted further with short wavelength irradiation to form ylide **4**. In contrast, laser flash photolysis of **1** in acetonitrile as well in nano crystal suspension of water at ambient temperature showed mainly formation of triplet vinylnitrene ^{3}**1N**, whereas laser flash photolysis of **2** revealed formation of ylide **4**. Thus, it can be concluded vinylnitrene ^{3}**1N** is not stable at cryogenic temperature and presumably intersystem crosses to ketenimine **3**. We will present and discuss the mechanism for the observed photoreactivity of **1** in solutions and cryogenic matrices, and support it with DFT calculations.

Interestingly, upon irradiation, the shape of crystal **2** changed significantly from needle-like to spherical bubbles. The crystal packing of **2** has channels that have a dimeter of 7.32 Å. Thus, we propose that these channels are responsible for the photodynamic behavior of **2**, and that **2** can rotate in the solid state. This notion was verified by studying a methyl substituted derivative of **2**, which does not display any photodynamic behavior and does not have any channels within its crystal lattice. We will discuss in more detail the photodynamic behavior of **2** and **1**.



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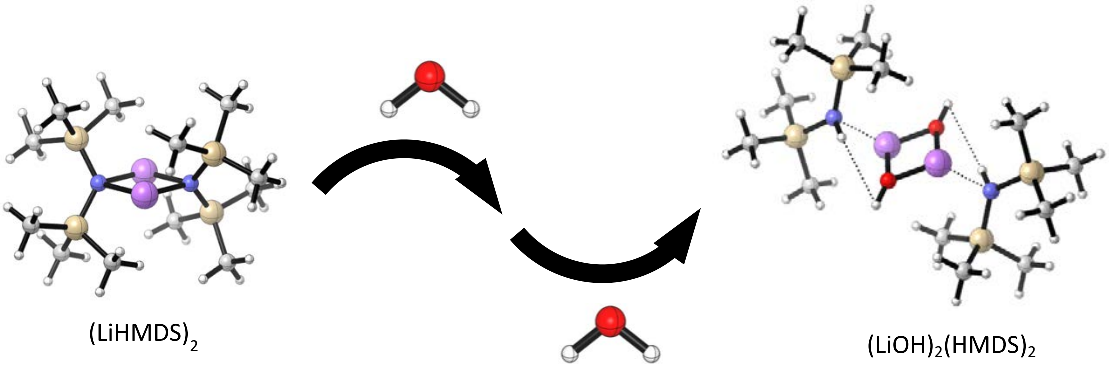
Reaction of Lithium Hexamethyldisilazide (LiHMDS) with Water at Ultracold Conditions

Svenja Jäger[1], Philipp Meyer[1], Kai-Stephan Feichtner[2], Stefan Henkel[1], Gerhard W. Schwaab[1], Viktoria H. Gessner[2] and Martina Havenith[1]

[1] Lehrstuhl für Physikalische Chemie II, Ruhr-Universität Bochum, 44780 Bochum, Germany

[2] Lehrstuhl für Anorganische Chemie II, Ruhr-Universität Bochum, 44780 Bochum, Germany

Highly reactive alkali metal amides play an important role in inorganic synthesis.[1-4] Due to their high reactivity with moisture, they are usually applied under strictly anhydrous reaction conditions to exclude undesired protonation or decomposition reactions. [5] This means that characterization of their specific properties, intermediates, and reaction mechanisms is challenging. We use a combined approach of Helium Nanodroplet Isolation Spectroscopy (HeNDI)[6-7]and DFT-calculations to show that the reaction of the model compound lithium hexamethyldisilazide (LiHMDS) with water is close to barrierless even at ultra-cold conditions (0.37 K). This so-called aggregation-induced-reaction results in formation of $(LiOH)_2(HMDS)_2$ upon stepwise addition of water. This implies that the large interaction energy of roughly 69 kJ mol^{-1} of $(LiHMDS)_2$ with water is sufficient to overcome the following reaction barriers, in spite of the rapid cooling rates in He nanodroplets.



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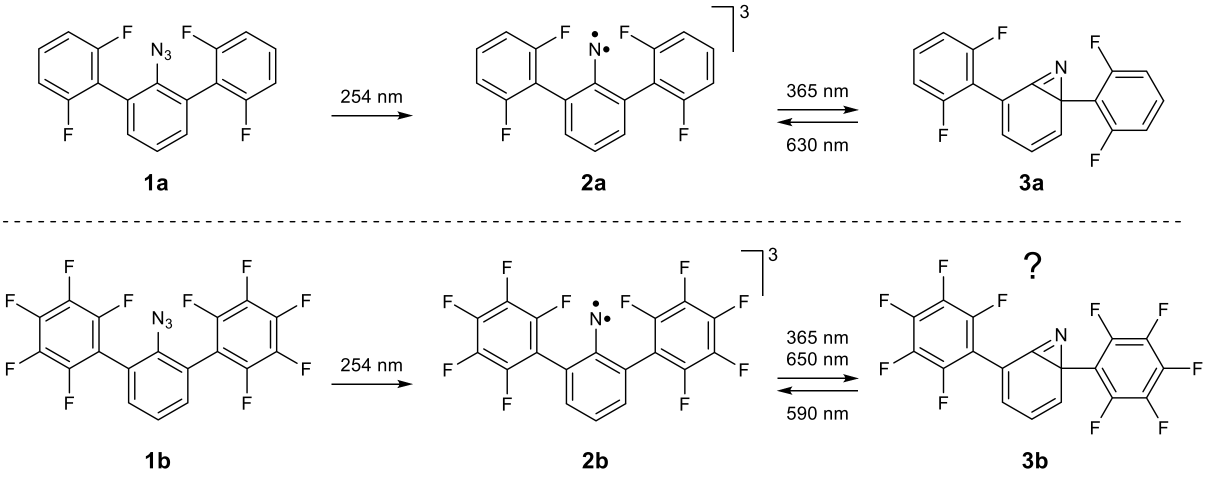
Synthesis and Reactivity of Fluorinated Terphenyl Nitrenes Beyond Cryogenic Conditions

Maurice Niehoff, Julien F. Rowen, Wolfram Sander

Ruhr-University Bochum, Faculty of Chemistry and Biochemistry, 44801 Bochum, Germany

Nitrenes are reactive intermediates with a robust triplet ground state and are of considerable interest in chemistry and biochemistry. Owing to their electron deficiency, nitrenes are fleeting species with a short lifetime at room temperature. The aim of this work is to design triplet nitrenes kinetically stabilized by steric hindrance but also by suppressing ring insertion by blocking the adjacent positions with fluorinated phenyl substituents.[1,2]

The parent *m*-terphenyl azide as well as two fluorinated derivatives **1a** and **1b** were synthesized and deposited under matrix isolation conditions in Ar at 3 K. Upon UV irradiation, triplet nitrenes **2a** and **2b** are generated and characterized by IR and UV spectroscopy. Secondary photochemistry of nitrenes **2a** and **2b** with 365 nm leads to the corresponding azirines **3a** and **3b**. Analogue experiments in KBr matrices were conducted and the thermal decay of the trapped nitrenes was monitored from 12 K to room temperature. Nitrenes **2a** and **2b** were found to persist in KBr matrices up to 70 and 120 K, respectively. At higher temperatures, a complex product mixture is obtained, containing amines and carbazoles, which are formed via H-abstraction and insertion of the nitrene center into the adjacent ring. Overall, KBr matrices allows immobilizing and extending the lifetime of sterically-hindered aryl nitrenes beyond cryogenic conditions.



Scheme 1: Photochemical synthesis and rearrangement of tetrafluoro and decafluoro terphenyl nitrene.

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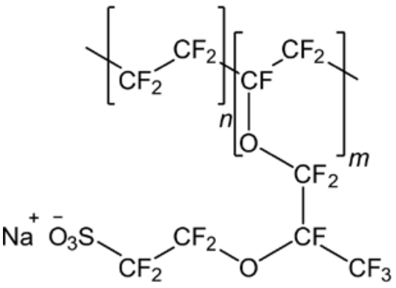
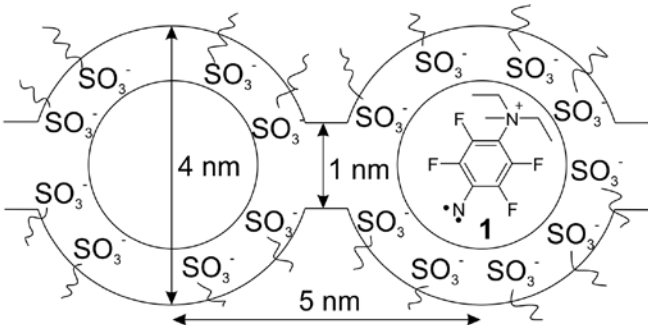
Stability of Triplet Arylnitrenes in Nafion Polymer at Ambient Temperatures

Adrián Portela González[1] **and Prof. Dr. Wolfram Sander**

[1] *Ruhr-Universität Bochum, Bochum, Germany*

Organic magnets possess properties (e.g. flexibility or transparency) that outcome those of conventional magnets. Triplet nitrenes exhibit strong magnetic properties and are of considerable interest as models for molecular magnets.[1] However, nitrenes are typically very short lived under ambient conditions so are usually trapped in low-temperature matrices.[2] Hence, the aim of this work is to generate persistent nitrenes at ambient conditions.





Nafion polymer was chosen as confinement media as its perfluorinated backbone would prevent undesired H-abstraction by nitrenes. Cationic ammonium groups were inserted into nitrene precursors such as 2,3,5,6-tetrafluorophenyl azide to facilitate the attachment to Nafion. Irradiation with UV light of cationic azides embedded into Nafion^{-}Na^{+} affords the corresponding nitrene in high yields. Typical byproducts such as azirines or ketenimines were not detected during photolysis or annealing. The nitrene stability was monitored by UV–vis, IR and EPR spectroscopy at different temperatures. Nitrene **1** is fully persistent in Nafion up to 200 K and survived for several hours at RT. The decay of nitrene **1** was observed to follow second-order kinetics, suggesting that dimerization is the main deactivation channel in correspondence with the spectroscopic data. Bulkier groups like perflurophenyl are expected to further extend the lifetime of the nitrene at RT by hampering its dimerization. Persistent nitrenes at room temperature could be great candidates as building blocks for organic magnets.

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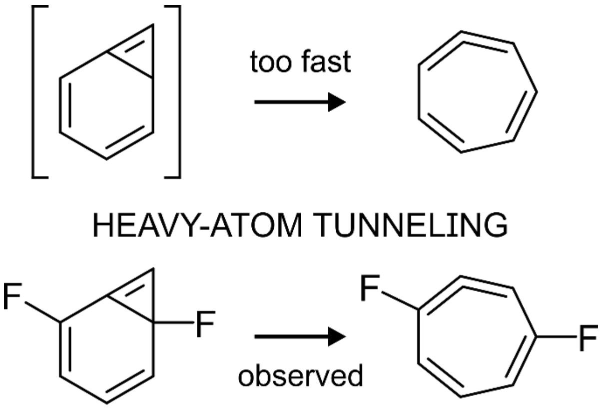
Heavy-Atom Tunneling in Bicyclo[4.1.0]hepta-2,4,6-trienes

Melania Prado Merini,[1] Tim Schleif,[2] and Wolfram Sander[1]

[1]Lehrstuhl für Organische Chemie II, Ruhr-Universität Bochum, 44780 Bochum, Germany
[2]Department of Chemistry, Yale University, New Haven, CT 06520, USA

Bicyclo[4.1.0]hepta-2,4,6-triene has been proposed as the primary intermediate in the rearrangement of phenylcarbene to cyclohepta-1,2,4,6-tetraene, but despite many efforts, it has remained elusive until today. Even under cryogenic conditions, the characterization of this highly strained bicycloheptatriene has not been achieved, as the ring expansion occurs via rapid heavy-atom tunneling. Fluorination of the two *ortho*-positions of the phenyl ring of phenylcarbene stabilizes 1,5-difluorobicyclo[4.1.0]hepta-2,4,6-triene enough to be detected under the conditions of matrix isolation. However, this benzocyclopropene is only metastable and in argon matrices at 3 K rearranges via heavy-atom tunneling to the corresponding cycloheptatetraene.



Trapping of 1,5-difluorobicyclo[4.1.0]hepta-2,4,6-triene by *ortho*-difluorination constitutes the first example of the capture and characterization of a highly strained benzocyclopropene as the long-sought intermediate in the photochemical rearrangement of phenylcarbenes to cycloallenes.

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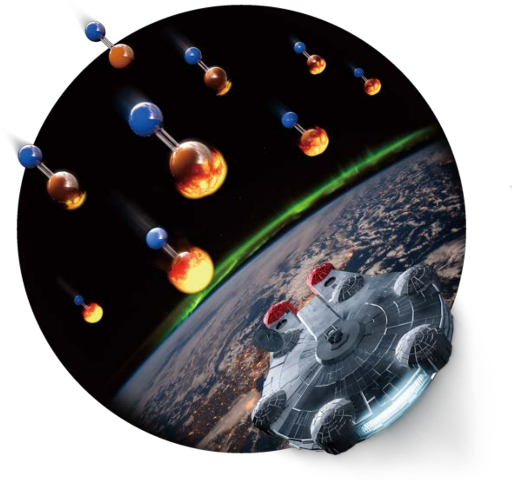
In Pursuit of Low-Valent Pnictogen Species

W. Qian,[1] **R. C. Wende,**[1] **P. R. Schreiner,**[1] **and A. Mardyukov**[1]

[1]*Institute of Organic Chemistry, Justus-Liebig University Giessen, 35392 Giessen, Germany*

As the pivotal elements in life, synthetic chemistry, and materials science, low-valent pnictogens have attracted broad attention. However, due to their high reactivity, there are still many species that have long eluded isolation and spectroscopic identification, thus making them elusive. The poster reports a selective preparation of metastable phosphorus mononitride (PN) in the gas phase, which is the highest number of detections for phosphorus-bearing interstellar species in star-forming regions. Its photo-induced recombination with ortho-benzoquinone in cryogenic matrices to covalently bonded (*o*-phenyldioxyl)-λ^5-phosphinonitrile discloses the first observed reactivity of PN towards organic molecules.[1] Besides, phenylarsinidene, a monovalent arsenic compound and the heavier analogue of phenylnitrene and phenylphosphinidene, was prepared and spectroscopically characterized. Oxidation by molecular oxygen led to the formation of hitherto unknown dioxophenylarsine, the arsenic analogue of nitrobenzene. In addition, *anti*-phenyldioxylarsinene was trapped as an intermediate, with different reactivity from that of the reactions of phenylphosphinidene and phenylnitrene with molecular oxygen.[2] Our discoveries of low-valent pnictogen species contribute to the knowledge of fundamental chemistry and provide new entry points for their applications in synthetic chemistry.



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Investigation of Fluorenyl-based Reactive Intermediates

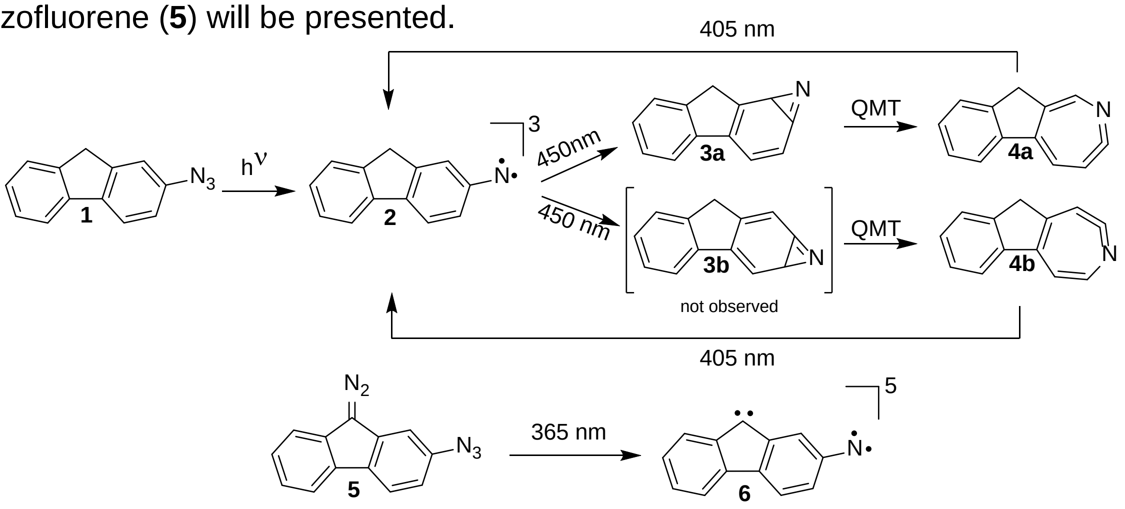
Julien F. Rowen[1], **Frederike Beyer**[1], **Tim Schleif**[2] **and Wolfram Sander**[1]

[1]Ruhr-Universität Bochum, 44780 Bochum, Germany
[2]Yale University, New Haven, Connecticut 06511, United States

Carbenes and nitrenes, due to their unpaired electrons in the triplet state, might serve as promising candidates for the development of organic magnets.[1] In order to study these fleeting molecules, they can be prepared e.g. photochemically from their precursors in a matrix consisting of solidified noble gases at cryogenic temperatures and then characterized by FT-IR, UV/Vis or EPR spectroscopy.

Here, the successful isolation of two fluorenyl-based reactive intermediates, 2-nitrenofluorene (**2**) and 2-nitreno-9-fluorenylidene (**6**), and their photochemistries in argon matrices are described. The triplet 2-nitrenofluorene (**2**) rearranges upon irradiation to the two ketenimine isomers **4a** and **4b**. However, in contrast to previous studies in solution, only the intermediately formed benzazirine isomer **3a** was detected and its rearrangement to the corresponding ketenimine **4a** by heavy-atom tunneling could be followed by kinetics measurements. Comparison of these results with DFT calculations suggests that the tunneling process of **3b** might be too fast to be resolved by matrix isolation measurements, thus explaining the discrepancy between solution-phase and matrix isolation measurements. Furthermore, the substituent effect potentially stemming from the fluorenyl moiety and resulting in the vastly different tunneling kinetics will be discussed.

Secondly, an interesting fluorenyl-based high-spin carbenonitrene **6** was isolated. Due to ferromagnetic coupling of the nitrene and carbene centers, a quintet ground state was verified by IR and EPR spectroscopy. Furthermore, indications for the mechanism under which this species is formed from the precursor 2-azido-9-diazofluorene (**5**) will be presented.



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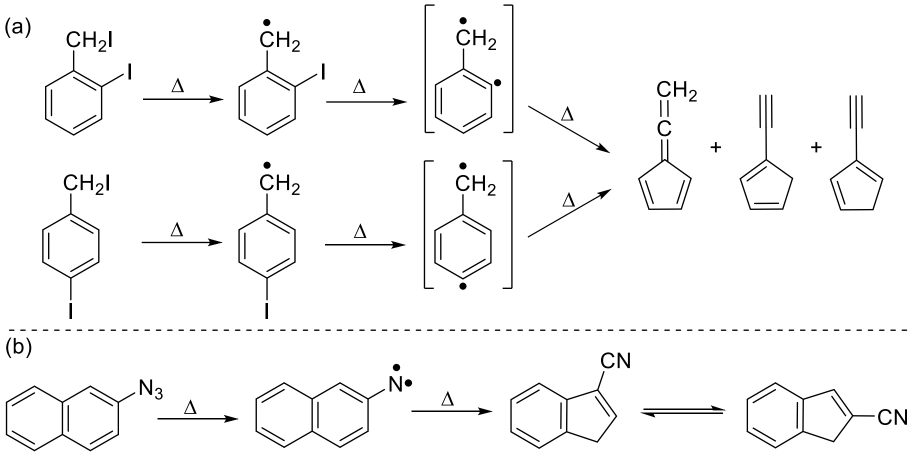
Gas phase thermal rearrangement of astrochemical relevant species: Threshold photoelectron and matrix isolation spectroscopic study

Mayank Saraswat[1], **Adrian Portela-Gonzalez**[1], **Enrique Mendez-Vega**[1], **Ginny Karir**[1], **Patrick Hemberger**[2], **and Wolfram Sander**[1]

[1]Ruhr-Universität Bochum, 44780 Bochum, Germany
[2]Paul Scherrer Institut (PSI), CH-5232 Villigen, Switzerland

Acquiring gas-phase energetic data on neutral and ion species is of great importance to support astrochemical observations but also to rationalize the photochemical and thermal formation of complex organic molecules in extreme environments. A variety of PAHs and PANHs have been recently detected in the ISM.[1] In this study, we combine mass-selective threshold photoelectron (ms-TPE) spectroscopy in the gas phase with matrix isolation IR spectroscopy in cryogenic matrices to elucidate the thermal decomposition of 2- and 4-iodobenzyl iodide (Scheme 1a) and 2-naphthylazide (Scheme 1b) via flash vacuum pyrolysis (FVP).[2] The adiabatic ionization energies (AIE) of involved reactive intermediates and their thermal rearrangement products were determined. Temperature dependent pyrolytic conditions were used to obtain different ratios of thermal rearrangement products. In addition, the ms-TPE spectra also allows to experimentally determine singlet-triplet ($\Delta E_{S\text{-}T}$) and doublet-quartet ($\Delta E_{D\text{-}Q}$) energy gaps of radical cations. Such isomer-specific spectroscopic and thermodynamic data are valuable not only for astrochemical models, but also for benchmarking theoretical methods.



Scheme 1. Pyrolytic route to (a) toluene diradicals and (b) 2-naphthylnitrene.

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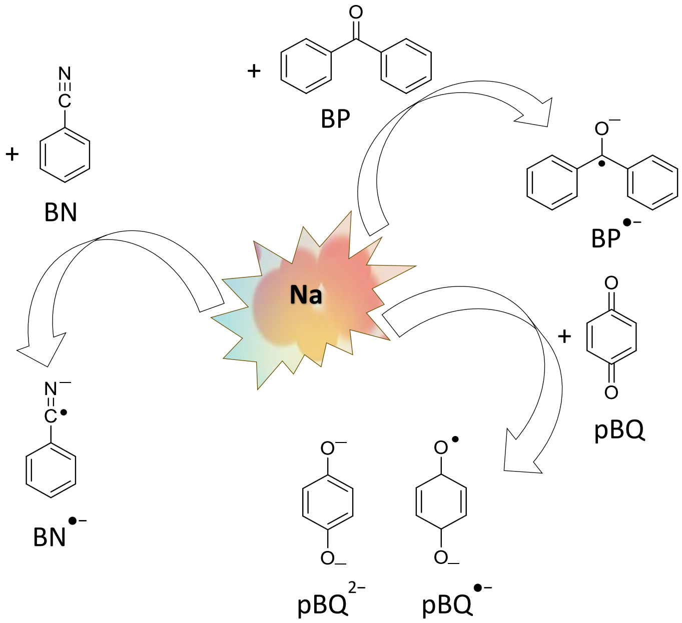
Radical Anions: Carbonyl versus Cyano compounds

Shubhra Sarkar, Ankit Somani, Wolfram Sander*

Lehrstuhl für Organische Chemie II, Ruhr-Universität Bochum, 44801 Bochum, Germany.

Email: shubhra.sarkar@rub.de

Stable radical anions (RA) are quite important intermediates in several chemical and biological processes. However, generating persistent RAs can be quite challenging. Recently, Na has been used as the source of electrons to produce RAs by depositing them with organic compounds in a stream of inert gas such as Ar onto a cold spectroscopic window. The current investigation will compare the RAs of carbonyl with cyano compounds emphasising the generation, stabilities, and the corresponding IR and UV-vis spectra at low temperatures. The co-condensation of Na with the organic compound led to the trapping of the RA and sometimes, a dianion, of the respective organic compound. Here, benzonitrile (BN, gas phase electron affinity, EA is 0.19 eV) is compared with benzophenone (BP, EA is 0.65 eV) and *p*-benzoquinone (pBQ, EA is 1.80 eV). Hence, for benzonitrile and benzophenone, only the RA was observed experimentally, however, the dianion of the latter was also trapped in addition to the corresponding RA. Interestingly, the RA of benzonitrile ($BN^{\bullet-}$) was stable to the annealing temperatures (20 – 35 K) which aided in probing its solvation in water, while the RAs of the carbonyl compounds were labile to such temperatures and hence could not be probed.

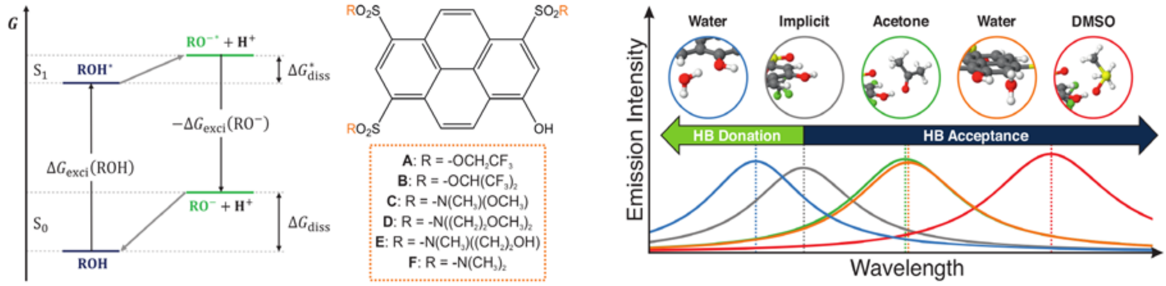


Going Beyond Implicit Solvent Effects on Hydroxypyrene Photoacids

<u>N. Sülzner</u>[1] and C. Hättig[1]

[1]Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, Bochum, Germany

Photoacids, i.e., molecules that exhibit an acidity increase upon electronic excitation, have received wide attention as molecular probes for the study of proton-transfer reactions. In this contribution, we apply the Förster cycle (Fig. 1a) to determine $\Delta\text{p}K_\text{a}$—the $\text{p}K_\text{a}$ jump upon excitation—for Jung's hydroxypyrene super-photoacids (Fig. 1b). In the course of this theoretical spectroscopy, UV/Vis absorption and fluorescence emission energies have been computed using the second-order wavefunction methods ADC(2) and CC2 in combination with the conductor-like screening model (COSMO), an (implicit) continuum solvation model. First, we show that very good results—in terms of accuracy with respect to experimental band maxima—are already obtained using CC2 in combination with pure COSMO in acetone [1]. In fact, these results are even better than in the previously studied DMSO [2]. Moreover, a comparison with TDDFT results indicates a strong dependence on contributions from exact exchange. Second, the need to go beyond implicit solvation by incorporating explicit solvent molecules in the first solvation shell is investigated in different solvent environments (Fig. 1c). It is shown that already one explicit solvent molecule yields an excellent agreement with the experiments for the aprotic solvents acetone and DMSO, whereas the situation is more involved in the protic solvent water. Finally, previous experimental studies in acetone–water mixtures [3] are complemented by modeling the experimentally observed peak progression in the UV/Vis absorption spectra, which can only be explained based on explicit solvent effects.



(a) Förster Cycle **(b)** Molecular Structures **(c)** Explicit Solvent Effects

Figure 1: Förster cycle, molecular structures, and explicit solvent effects for Jung's photoacids.

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Organic Hydroperoxide Triplet Reactivity for Releasing O_2 Utilizing Photochemical Reactions

F. J. Wasson[1], and A. D. Gudmundsdottir[1]

Irradiation of crystalline azido compounds releases inert nitrogen gas into their crystal lattices as photoproducts are formed, the buildup of gas pressure causes the crystals to have spectacular photodynamic response, which is controlled by their crystal packing arrangements.[1] In contrast, light-induced release of singlet or triplet oxygen molecules, can be expected to be different as both configurations of the oxygen molecules are reactive and can therefore be trapped to react before escaping the crystal lattice. However, many important applications for releasing oxygen from the solid-state include breathing cannulas, gas expansion, organic synthesis, and ROS biological drugs. Because endo- and hydroperoxides are photolabile although the photochemical reactions mechanism has not been determined,[2] we embarked upon investigating the photoreactivity trityl hydroperoxide (**1**) in both solution and the solid state. Irradiation of **1** yields two products: benzophenone (**2**) and phenol (**3**) in solution and crystals. Laser flash photolysis of **1** in solution shows a long-lived intermediate with λ_{max} at 320 nm that is assigned to Ph_3C radical and a short-lived intermediate with λ_{max} 320, 520, and 620 nm, which can be assigned to the triplet excited state of **1** or Ph_3CO radical. We are performing quenching studies to better characterize the intermediates observed in the transient spectroscopy. Irradiation of crystals of **1** causes their surface to turn yellow and release of gas molecules. The crystal structure of **1** shows that it packs into the crystal lattice in such a manner that they fit into each other.[3] We will discuss how the crystal lattice affects the reaction mechanisms and oxygen release.

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Investigating the Photodissociation Dynamics of CH_2Br with VMI

L. Wohlfart, **C. Matthaei and Ingo Fischer**

Julius-Maximilians-Universität, Institute for Physical and Theoretical Chemistry, Würzburg, Germany

Bromomethyl belongs to the class of organic halogen radicals. Therefore, it can potentially influence the atmosphere by reacting with the ozone layer and causing its depletion similar to HCFCs. The photoionization of bromomethyl was already investigated by several groups, including Steinbauer and coworkers.[1] They determined the ionization energy and structure with VUV synchrotron radiation and investigated the dissociative photoionization. To obtain further insights into the dissociation of bromomethyl, we analyzed the fragments of the radical using velocity map imaging (VMI).

CH_2Br-NO_2 was used as a precursor for the halogenated methyl radical, because the weaker C-NO_2 bond can be cleaved through pyrolysis. Subsequently, laser light with 235 nm was deployed to dissociate the formed CH_2Br radical. The major dissociation pathway gave the methylene and bromine fragments which were detected with SPI at 118 nm and [1+1']-REMPI at 356 nm respectively. With velocity map ion imaging, the translational kinetic energy distribution of the photofragments was determined. The recorded images of the bromine and methylene photofragments showed an anisotropic distribution, implying a direct dissociation.

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Theoretical study of the cyclopentadienylidene carbene and its reactivity on metal surfaces

Y. Liu[1], J. Mieres-Perez[1] and E. Sanchez-Garcia[1]

[1] *Computational Bioengineering, Technical University Dortmund, Dortmund, Germany*

Carbenes play a crucial role in many chemical and physical processes. However, the study of carbene interactions and reactivity on metal surfaces is challenging due to the unique characteristics of carbenes. In this study, we employ theoretical approaches to examine the interactions of cyclopentadienylidene carbene with three distinct metal surfaces (Ag111, Cu111, and Co111), both in the presence and absence of water. To simulate the behavior of this carbene, we apply plane-wave DFT calculations and pseudopotentials.