REPORT DOCUMENTATION PAGE

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17-01-2023	Final Report	1-Apr-2017 - 30-Oct-2022

4. TITLE AND SUBTITLE

Final Report: Atmospheric Aerosols as Chemical Micro Reactors in the Environment

5a. CONTRACT NUMBER: W911NF-17-1-0115

5b. GRANT NUMBER:

5c. PROGRAM ELEMENT NUMBER: 611102

5d. PROJECT NUMBER:

5e. TASK NUMBER:

5f. WORK UNIT NUMBER:

6. AUTHORS

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES

University of Colorado - Boulder
3100 Marine Street, Room 481
572 UCB
Boulder, CO 80303 -1058

8. PERFORMING ORGANIZATION REPORT NUMBER

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U.S. Army Research Office
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11. SPONSOR/MONITOR'S REPORT NUMBER(S): 70381-BB.21

12. DISTRIBUTION AVAILIBILITY STATEMENT

Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF: a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
UU	UU	UU	UU		Veronica Vaida
					19b. TELEPHONE NUMBER
					303-492-8605

RPPR Final Report
as of 18-Jan-2023

Agency Code: 21XD

Proposal Number: 70381BB **Agreement Number: W911NF-17-1-0115**

INVESTIGATOR(S):

Name: Ph.D. Veronica Vaida
Email: vaida@colorado.edu
Phone Number: 3034928605
Principal: Y

Organization: **University of Colorado - Boulder**
Address: 3100 Marine Street, Room 481, Boulder, CO 803031058
Country: USA

DUNS Number: 007431505 EIN: 846000555
Report Date: 30-Jan-2023 Date Received: 17-Jan-2023
Final Report for Period Beginning 01-Apr-2017 and Ending 30-Oct-2022
Title: Atmospheric Aerosols as Chemical Micro Reactors in the Environment
Begin Performance Period: 01-Apr-2017 **End Performance Period:** 30-Oct-2022
Report Term: 0-Other

Submitted By: Ph.D. Veronica Vaida Email: vaida@colorado.edu
Phone: (303) 492-8605

Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees: 0 **STEM Participants:**

Major Goals: See the objectives described in the uploaded document on scientific accomplishments

Accomplishments: See report

Training Opportunities: This interdisciplinary project provided many opportunities for education and outreach to a group of diverse undergraduate and graduate students, postdoctoral fellows and visitors, including international collaborators. Work at the interface of physical chemistry and environmental science was carried out with complementary experimental and computational methods. Students in the group were trained in these complementary approaches. International interactions occurred in collaboration with and participation of researchers in the CESAM group, LISA, Universite? de Paris-Est, University of Copenhagen and Aarhus University in Denmark provided an international context for young researchers involved in this project.

Dr. Rebecca Rapf, Assistant professor, Trinity University, San Antonio, TX visited our group with two undergraduate researchers performing surface reflection spectroscopy in the summer of 2022.

Materials were prepared and presented at the Travis Lake Academy for K-12 pupils on diversity in science.

Results Dissemination: The results of this study were disseminated through open access peer reviewed publications. The 20 publications acknowledging support from this grant are uploaded into the report Products section.

Two years of covid restrictions on scientific meetings slowed down the number of presentations from the PI and group members. However, results of this research were presented in person and remotely at national and international meetings by the PI and group members. These included Gordon Research Conferences, Gordon Research Seminars, American Chemical Society Meetings, Simons Foundation Conference, American Institute of Chemists, invited talks at universities (Stanford, Yale, University of Alberta, Canada, Berkeley) as well as international presentations (UK Center for Doctoral training in Aerosol Science, IAMS Taipei, Taiwan, Czech Academy of Sciences) as well as by graduate students (Gordon Research Conferences) and postdoctoral fellows (ACS) from the group.

Honors and Awards: Veronica Vaida Festschrift Special Issue: Journal of Physical Chemistry
Contributed papers at the interface of physical chemistry and environmental science

National Academy of Sciences elected member 2020

ACS Irving Langmuir Award in Chemical Physics 2020

2020 Wilbur Lucius Cross Medal presented by the Yale Graduate School Alumni Association

The 2021 Chemical Pioneer Award- the American Institute of Chemists.

Rebecca Rapf (Vaida group PhD 2017): Astrobiology: Maggie C. Turnbull Astrobiology Community Service Award 2018

Protocol Activity Status:

Technology Transfer: Nothing to Report

ARTICLES:

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: ACS Earth and Space Chemistry
Publication Identifier Type: DOI Publication Identifier: 10.1021/acsearthspacechem.7b00054
Volume: 1 Issue: 6 First Page #: 345
Date Submitted: 8/29/17 12:00AM Date Published: 7/1/17 12:00PM
Publication Location:
Article Title: Ultraviolet Spectroscopy of the Gas Phase Hydration of Methylglyoxal
Authors: Jay A. Kroll, Anne S. Hansen, Kristian H. Møller, Jessica L. Axson, Henrik G. Kjaergaard, Veronica Vaid
Keywords: Methylglyoxal, geminal diol, ultraviolet, electronic spectrum, atmospheric chemistry, gas phase
Abstract: The gas phase ultraviolet spectrum and stability of 1,1-dihydroxyacetone (the geminal diol of methylglyoxal) are investigated using spectroscopic and computational methods. Experimental gas phase electronic spectra recorded in the ultraviolet?visible range were used to follow the hydration of methylglyoxal. We show that upon the addition of water, ethylglyoxal hydrates to form the geminal diol. The electronic spectra of methylglyoxal and its geminal diol conformers were calculated using TD-DFT and LR-CC methods to facilitate experimental peak assignments. The lowest energy electronic transition of the diol is experimentally measured and compared with the results of the theoretical calculations. We find that upon formation of the diol, the lowest-energy transition of methylglyoxal (centered around ?430 nm) vanishes, and the remaining transitions, including the methylglyoxal diol absorptions (?max = 240 nm), fall outside the available solar actinic flux in the troposphere.
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Journal of Physical Chemistry A
Publication Identifier Type: DOI Publication Identifier: 10.1021/acs.jpca.7b08192
Volume: 121 Issue: 44 First Page #: 8368
Date Submitted: 6/18/18 12:00AM Date Published: 10/14/17 6:00AM
Publication Location: Washington, DC
Article Title: pH Dependence of the Aqueous Photochemistry of ?-Keto Acids
Authors: Rebecca J. Rapf, Michael R. Dooley, Keaten Kappes, Russell J. Perkins, Veronica Vaida
Keywords: ?-Keto acids, aqueous photochemistry, aerosols
Abstract: ?-Keto acids are important, atmospherically relevant species, and their photochemistry has been considered in the formation and processing of aerosols. Despite their atmospheric relevance, the photochemistry of these species has primarily been studied under extremely low pH conditions. Using a variety of analytical techniques, we characterize the extent of hydration and deprotonation for solutions of two ?-keto acids, pyruvic acid and 2-oxooctanoic acid, as a function of pH. We find that changes in the initial solution composition govern the accessibility of different photochemical pathways, resulting in slowed photolysis under high pH conditions and a shift in photoproducts that can be predicted mechanistically.
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Journal of Physical Chemistry A
Publication Identifier Type: DOI Publication Identifier: 10.1021/acs.jpca.7b08192
Volume: 121 Issue: 44 First Page #: 8368
Date Submitted: 6/18/18 12:00AM Date Published: 10/14/17 6:00PM
Publication Location: Washington, DC
Article Title: pH Dependence of the Aqueous Photochemistry of ?-Keto Acids
Authors: Rebecca Rapf, Michael Dooley, Keaten Kappes, Russell Perkins, and Veronica Vaida
Keywords: ?-Keto acids, aqueous photochemistry, aerosols
Abstract: ?-Keto acids are important, atmospherically relevant species, and their photochemistry has been considered in the formation and processing of aerosols. Despite their atmospheric relevance, the photochemistry of these species has primarily been studied under extremely low pH conditions. Using a variety of analytical techniques, we characterize the extent of hydration and deprotonation for solutions of two ?-keto acids, pyruvic acid and 2-oxooctanoic acid, as a function of pH. We find that changes in the initial solution composition govern the accessibility of different photochemical pathways, resulting in slowed photolysis under high pH conditions and a shift in photoproducts that can be predicted mechanistically.
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: The Journal of Physical Chemistry A
Publication Identifier Type: DOI Publication Identifier: 10.1021/acs.jpca.8b03524
Volume: 122 Issue: 18 First Page #: 4465
Date Submitted: 6/18/18 12:00AM Date Published: 4/1/18 6:00AM
Publication Location: Washington, DC
Article Title: Atmospheric Hydroxyl Radical Source: Reaction of Triplet SO
Authors: Jay A. Kroll, Benjamin N. Frandsen, Henrik G. Kjaergaard, Veronica Vaida
Keywords: UV radiation, hydroxyl radical, sulfur, SO2
Abstract: The reaction of electronically excited triplet state sulfur dioxide (3SO2) with water was investigated both theoretically and experimentally. The quantum chemical calculations find that the reaction leads to the formation of hydroxyl radical (OH) and hydroxysulfinyl radical (HOSO) via a low energy barrier pathway. Experimentally the formation of OH was monitored via its reaction with methane, which itself is relatively unreactive with 3SO2, making it a suitable probe of OH production from the reaction of 3SO2 and water. This reaction has implications for the formation of OH in environments that are assumed to be depleted in OH, such as volcanic plumes. This reaction also provides a mechanism for the formation of OH in planetary atmospheres with little or no oxygen (O2) or ozone (O3) present.
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
Acknowledged Federal Support: **Y**

Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: ACS Central Science
Publication Identifier Type: DOI Publication Identifier: 10.1021/acscentsci.8b00124
Volume: 4 Issue: 5 First Page #: 624
Date Submitted: 6/18/18 12:00AM Date Published: 4/1/18 12:00PM
Publication Location: Washington, DC
Article Title: Environmental Processing of Lipids Driven by Aqueous Photochemistry of ?-Keto Acids
Authors: Rebecca J. Rapf, Russell J. Perkins, Michael R. Dooley, Jay A. Kroll, Barry K. Carpenter, Veronica Vaid
Keywords: photolysis, ?-keto acids, radical initiators, molecular complexity
Abstract: Sunlight can initiate photochemical reactions of organic molecules though direct photolysis, photosensitization, and indirect processes, often leading to complex radical chemistry that can increase molecular complexity in the environment. ?-Keto acids act as photoinitiators for organic species that are not themselves photoactive. Here, we demonstrate this capability through the reaction of two ?-keto acids, pyruvic acid and 2-oxooctanoic acid, with a series of fatty acids and fatty alcohols. We show for five different cases that a cross-product between the photoinitiated ?-keto acid and non-photoactive species is formed during photolysis in aqueous solution. Fatty acids and alcohols are relatively unreactive species, which suggests that ?-keto acids are able to act as radical initiators for many atmospherically relevant molecules found in the sea surface microlayer and on atmospheric aerosol particles.
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Proceedings of the National Academy of Sciences
Publication Identifier Type: DOI Publication Identifier: 10.1073/pnas.1717373114
Volume: 114 Issue: 47 First Page #: 12359
Date Submitted: 6/18/18 12:00AM Date Published: 11/1/17 12:00PM
Publication Location: Washington, DC
Article Title: Prebiotic phosphorylation enabled by microdroplets
Authors: Veronica Vaida
Keywords: microdroplets, prebiotic, phosphorylation, accelerated reactions
Abstract: N/A- This is a commentary article.
Distribution Statement: 3-Distribution authorized to U.S. Government Agencies and their contractors
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published

Journal: The Journal of Physical Chemistry A
Publication Identifier Type: DOI Publication Identifier: 10.1021/acs.jpca.8b04643
Volume: 122 Issue: 39 First Page #: 7782
Date Submitted: 11/13/18 12:00AM Date Published: 9/1/18 6:00AM
Publication Location:

Article Title: Reactivity of Electronically Excited SO2 with Alkanes

Authors: Jay A. Kroll, Benjamin N. Frandsen, Rebecca J. Rapf, Henrik G. Kjaergaard, Veronica Vaida

Keywords: photoinitiated reactions, SO2, alkanes, hydrogen abstraction

Abstract: We studied the reaction of electronically excited sulfur dioxide in the triplet state (3SO2) with a variety of alkane species, including propane, n-butane, isobutane, n-pentane, n-hexane, cyclohexane, n-octane, and n-nonane. Reaction rate constants for the photoinitiated reaction of SO2 with all of these species were determined and found to be in the range from 3.7 × 10?13 to 5.1 × 10?12cm3molecule?1s?1. We found that reaction proceeds via a hydrogen abstraction to form HOSO• and organic radical (R•) species and that reactivity is correlated with the energy required to break a C?H bond and the length of the alkane chain. Abstraction rates were found to be fastest for reaction with hydrogen on a tertiary carbon. Similarly, abstraction from secondary carbons is found to be faster than from primary carbons. The reactivity of 3SO2 with alkanes increases with chain length as additional secondary carbons are added.

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Journal: The Journal of Physical Chemistry A
Publication Identifier Type: DOI Publication Identifier: 10.1021/acs.jpca.8b10224
Volume: 123 Issue: 5 First Page #: 983
Date Submitted: 6/19/19 12:00AM Date Published: 1/11/19 7:00AM
Publication Location:

Article Title: Heterogeneous Interactions between Gas-Phase Pyruvic Acid and Hydroxylated Silica Surfaces: A Combined Experimental and Theoretical Study

Authors: Yuan Fang, Dominika Lesnicki, Kristin J. Wall, Marie-Pierre Gaigeot, Marialore Sulpizi, Veronica Vaida,

Keywords: pyruvic acid, silica, surface, hydrogen bond, gas-phase, FTIR

Abstract: The adsorption of gas-phase pyruvic acid (CH3COCOOH) on hydroxylated silica particles has been investigated at 296 K using transmission Fourier transform infrared (FTIR) spectroscopy and theoretical simulations. Under dry conditions (<1% relative humidity, RH), both the trans–cis (Tc) and trans–trans (Tt) pyruvic acid conformers are observed on the surface as well as the (hydrogen bonded) pyruvic acid dimer. The detailed surface interactions were further understood through ab initio molecular dynamics simulations. Under higher relative humidity conditions (above 10% RH), adsorbed water competes for surface adsorption sites. Adsorbed water is also observed to change the relative populations of the different adsorbed pyruvic acid configurations. Overall, this study provides valuable insights into the interaction of pyruvic acid with hydroxylated silica surfaces on the molecular level from both experimental and theoretical analyses. Furthermore, these results highlight the importance ...

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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: The Journal of Physical Chemistry A
Publication Identifier Type: DOI Publication Identifier: 10.1021/acs.jpca.9b10613
Volume: 124 Issue: 7 First Page #: 1240
Date Submitted: 8/12/20 12:00AM Date Published: 1/1/20 7:00AM
Publication Location: United States
Article Title: Conformer-Specific Photolysis of Pyruvic Acid and the Effect of Water
Authors: Sandra L. Blair, Allison E. Reed Harris, Benjamin N. Frandsen, Henrik G. Kjaergaard, Edouard Pangui, I
Keywords: Pyruvic Acid, photolysis, water surface chemistry

Abstract: The surface chemistry and photochemistry of gas-phase pyruvic acid (CH3COCOOH) on two oxides, Al2O3 and TiO2, have been investigated using transmission Fourier transform infrared spectroscopy and mass spectrometry. At 298 K, the carboxylic acid group within pyruvic acid is found to react with surface hydroxyl groups (M?OH, M = Al, Ti) to yield pyruvate as a predominant adsorbed organic species. Upon broad-band UV irradiation (? > 280 nm), there is a loss of adsorbed pyruvate with the concomitant formation of new products. The photochemical loss of pyruvate is higher on TiO2 than on Al2O3 indicating that the photochemistry is enhanced on the surface of a semiconductor oxide, TiO2, compared with an insulator oxide, Al2O3. Analysis of products extracted from the surface with mass spectrometry shows the formation of several new compounds. This includes zymonic acid, which is found to be present under both dark and light conditions, and other higher-molar-mass oligomeric species such as ..

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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: The Journal of Physical Chemistry A
Publication Identifier Type: DOI Publication Identifier: 10.1021/acs.jpca.9b06563
Volume: 123 Issue: 35 First Page #: 7661
Date Submitted: 8/12/20 12:00AM Date Published: 8/1/19 6:00PM
Publication Location: United States
Article Title: Chemistry and Photochemistry of Pyruvic Acid Adsorbed on Oxide Surfaces
Authors: Michael R. Alves, Yuan Fang, Kristin J. Wall, Veronica Vaida, Vicki H. Grassian
Keywords: pyruvic Acid, oxide surface chemistry, photochemistry

Abstract: The surface chemistry and photochemistry of gas-phase pyruvic acid (CH3COCOOH) on two oxides, Al2O3 and TiO2, have been investigated using transmission Fourier transform infrared spectroscopy and mass spectrometry. At 298 K, the carboxylic acid group within pyruvic acid is found to react with surface hydroxyl groups (M?OH, M = Al, Ti) to yield pyruvate as a predominant adsorbed organic species. Upon broad-band UV irradiation (? > 280 nm), there is a loss of adsorbed pyruvate with the concomitant formation of new products. The photochemical loss of pyruvate is higher on TiO2 than on Al2O3 indicating that the photochemistry is enhanced on the surface of a semiconductor oxide, TiO2, compared with an insulator oxide, Al2O3. Analysis of products extracted from the surface with mass spectrometry shows the formation of several new compounds. This includes zymonic acid, which is found to be present under both dark and light conditions, and other higher-molar-mass oligomeric species such as ..

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Journal: Physical Chemistry Chemical Physics
Publication Identifier Type: DOI Publication Identifier: 10.1039/D0CP05650B
Volume: 23 Issue: 8 First Page #: 4555
Date Submitted: 7/16/21 12:00AM Date Published:
Publication Location: Great Britain
Article Title: The primary photo-dissociation dynamics of lactate in aqueous solution: decarboxylation prevents dehydroxylation
Authors: Jan Thøgersen, Veronica Vaida, Mikkel Bregnhøj, Tobias Weidner, Frank Jensen
Keywords: Photochemistry, solution, decarboxylation
Abstract: Lactic acid, a relevant molecule in biology and the environment, is an ?-hydroxy acid with a high propensity to form hydrogen bonds, both internally and to other hydrogen-bond-accepting molecules. This work includes the novel recording of infrared spectra of gas-phase lactic acid using Fourier transform infrared spectroscopy, and the vibrational absorption features of lactic acid are assigned with the aid of computationally simulated vibrational spectra with anharmonic corrections. Theoretical chemistry methods are used to relate intramolecular hydrogen-bond strengths to the relative stability of lactic acid conformers. The formation of hydrogen-bonded lactic acid dimers and 1:1 water complexes is investigated by simulated vibrational spectra and calculated thermodynamic parameters for the lactic acid monomer and dimer and its water complex in the gas phase. The results of this study are discussed in the context of environmental chemistry with an emphasis on indoor environments.
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Journal: The Journal of Physical Chemistry A
Publication Identifier Type: DOI Publication Identifier: 10.1021/acs.jpca.0c09096
Volume: 125 Issue: 4 First Page #: 1036
Date Submitted: 7/16/21 12:00AM Date Published: 1/1/21 7:00AM
Publication Location: Washington, D.C., U.S.A.
Article Title: Chemistry and Photochemistry of Pyruvic Acid at the Air–Water Interface
Authors: Keaten J. Kappes, Alexandra M. Deal, Malte F. Jespersen, Sandra L. Blair, Jean-Francois Doussin, Mat
Keywords: Photodissociaiton, interface, liquids. solution chemistry, oligomers
Abstract: Interfacial regions are unique chemical reaction environments that can promote chemistry not found elsewhere. The air–water interface is ubiquitous in the natural environment in the form of ocean surfaces and aqueous atmospheric aerosols. Here we investigate the chemistry and photochemistry of pyruvic acid (PA), a common environmental species, at the air–water interface and compare it to its aqueous bulk chemistry using two different experimental setups: (1) a Langmuir–Blodgett trough, which models natural water surfaces and provides a direct comparison between the two reaction environments, and (2) an atmospheric simulation chamber (CESAM) to monitor the chemical processing of nebulized aqueous PA droplets. The results show that surface chemistry leads to substantial oligomer formation. The sequence begins with the condensation of lactic acid (LA), formed at the surface, with itself and with pyruvic acid, and LA + LA – H2O and LA + PA – H2O are prominent among the products in addition
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Journal: The Journal of Physical Chemistry A
Publication Identifier Type: DOI Publication Identifier: 10.1021/acs.jpca.0c09341
Volume: 125 Issue: 1 First Page #: 218
Date Submitted: 7/16/21 12:00AM Date Published: 12/1/20 7:00AM
Publication Location:
Article Title: Lactic Acid Spectroscopy: Intra- and Intermolecular Interactions
Authors: Benjamin N. Frandsen, Alexandra M. Deal, Joseph R. Lane, Veronica Vaida
Keywords: organic acids, oligomers, noncovalent chemistry
Abstract: Lactic acid, a relevant molecule in biology and the environment, is an ?-hydroxy acid with a high propensity to form hydrogen bonds, both internally and to other hydrogen-bond-accepting molecules. This work includes the novel recording of infrared spectra of gas-phase lactic acid using Fourier transform infrared spectroscopy, and the vibrational absorption features of lactic acid are assigned with the aid of computationally simulated vibrational spectra with anharmonic corrections. Theoretical chemistry methods are used to relate intramolecular hydrogen-bond strengths to the relative stability of lactic acid conformers. The formation of hydrogen-bonded lactic acid dimers and 1:1 water complexes is investigated by simulated vibrational spectra and calculated thermodynamic parameters for the lactic acid monomer and dimer and its water complex in the gas phase. The results of this study are discussed in the context of environmental chemistry with an emphasis on indoor environments.
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: The Journal of Physical Chemistry A
Publication Identifier Type: DOI Publication Identifier: 10.1021/acs.jpca.1c02864
Volume: 125 Issue: 23 First Page #: 4929
Date Submitted: 7/16/21 12:00AM Date Published: 5/1/21 12:00PM
Publication Location: Washington, D.C., U.S.A.
Article Title: Water–Air Interfaces as Environments to Address the Water Paradox in Prebiotic Chemistry: A Physical Chemistry Perspective
Authors: Alexandra M. Deal, Rebecca J. Rapf, Veronica Vaida
Keywords: photochemistry, peptides and proteins, interfaces
Abstract: The asymmetric water–air interface provides a dynamic aqueous environment with properties that are often very different than bulk aqueous or gaseous phases and promotes reactions that are thermodynamically, kinetically, or otherwise unfavorable in bulk water. Prebiotic chemistry faces a key challenge: water is necessary for life yet reduces the efficiency of many biomolecular synthesis reactions. This perspective considers water–air interfaces as auspicious reaction environments for abiotic synthesis. We discuss recent evidence that (1) water–air interfaces promote condensation reactions including peptide synthesis, phosphorylation, and oligomerization; (2) photochemistry at water–air interfaces may have been a significant source of prebiotic molecular complexity, given the lack of oxygen and increased availability of near-ultraviolet radiation on early Earth; and (3) water–air interfaces can promote spontaneous reduction and oxidation reactions, potentially providing protometabolic..
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Journal: Physical Chemistry Chemical Physics
Publication Identifier Type: DOI Publication Identifier: doi.org/10.1039/d1cp05345k
Volume: 24 Issue: First Page #: 6757
Date Submitted: 8/14/22 12:00AM Date Published:
Publication Location: United Kingdom
Article Title: Infrared Spectroscopy of 2-Oxo-Octanoic Acid in Multiple Phases
Authors: Keaton Kappes,Benjamin Frandsen, Veronica Vaida,
Keywords: Photochemistry, surface chemistry, keto acids
Abstract: Alpha-keto acids are environmentally and biologically relevant species whose chemistry has been shown to be influenced by their local environment. Vibrational spectroscopy provides useful ways to probe the potential inter- and intramolecular interactions available to them in several phases. We measure and compare the IR spectra of 2-oxo-octanoic acid (2OOA) in the gas phase, solid phase, and at the air–water interface. With theoretical support, we assign many of the vibrational modes in each of the spectra. In the gas phase, two types of conformers are identified and distinguished, with the intramolecularly H-bonded form being the dominant type, while the second conformer type identified does not have an intramolecular hydrogen bond. The van der Waals interactions between molecules in solid 2OOA manifest C–H and C[double bond, length as m-dash]O vibrations lower in energy than in the gas phase and we propose an intermolecular hydrogen bonding scheme for the solid phase. At the air–wate
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Journal of Physical Organic Chemistry
Publication Identifier Type: DOI Publication Identifier: doi.org/10.1002/poc.4316
Volume: Issue: First Page #: 1
Date Submitted: 8/14/22 12:00AM Date Published: 1/10/22 2:00PM
Publication Location: USA - online
Article Title: Lactic acid photochemistry following excitation of S0 to S1 at 220 to 250 nm
Authors: Alexandra M. Deal,Benjamin N. Frandsen, Veronica Vaida
Keywords: Alpha-keto acids, 2-oxo-octanoic acid, infrared spectroscopy
Abstract: Organic molecules, including ?-hydroxyacids, are ubiquitous in the natural environment. Often found at water-air interfaces, organic molecules can alter the structure of the interface or participate in interfacial chemistry. Despite their prevalence in the environment, the structure and ordering of ?-hydroxyacids has not been widely investigated at water-air interfaces and the impact of the hydrophobic tail length on structure has not been explored. Here, for the first time, we use Infrared Reflection-Absorption Spectroscopy to assess the vibrational structure of ?-hydroxyacids at a water surface as a function of surface partitioning and surface coverage. We study lactic acid, 2- hydroxyoctanoic acid, and 2-hydroxystearic acid which have 1 carbon, 6 carbon, and 16 carbon tails respectively. Vibrational features compared across the set of ?-hydroxyacids studied are used to determine the interaction of the polar headgroup with the water subphase and the ordering of the hydrophobic tail.
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Journal of Physical Chemistry
Publication Identifier Type: DOI Publication Identifier: doi.org/10.1021/acs.jpca.2c04462
Volume: 126 Issue: First Page #: 8280
Date Submitted: 1/14/23 12:00AM Date Published:
Publication Location: United States
Article Title: Infrared Reflection Absorption Spectroscopy of Hydroxyacids at the Water -Air Interface
Authors: Alexandra M. Deal, Veronica Vaida
Keywords: organic acids, aqueous surface reaction
Abstract: Organic molecules, including ?-hydroxyacids, are ubiquitous in the natural environment. Often found at water-air interfaces, organic molecules can alter the structure of the interface or participate in interfacial chemistry. Despite their prevalence in the environment, the structure and ordering of ?-hydroxyacids has not been widely investigated at water-air interfaces and the impact of the hydrophobic tail length on structure has not been explored. Here, for the first time, we use Infrared Reflection-Absorption Spectroscopy to assess the vibrational structure of ?-hydroxyacids at a water surface as a function of surface partitioning and surface coverage. We study lactic acid, 2- hydroxyoctanoic acid, and 2-hydroxystearic acid which have 1 carbon, 6 carbon, and 16 carbon tails respectively. Vibrational features compared across the set of ?-hydroxyacids studied are used to determine the interaction of the polar headgroup with the water subphase and the ordering of the hydrophobic tail.
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Publication Identifier Type: DOI Publication Identifier: doi.org/10.1021/acs.jpca.2c04873
Volume: 126 Issue: First Page #: 6908
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Article Title: Spectroscopy of Retinoic Acid at the Air-Water Interface
Authors: Benjamin N. Frandsen, Veronica Vaida
Keywords: retinoic acid, spectroscopy of organic acids, air-water interface
Abstract: The spectroscopy of all-trans-retinoic acid (ATRA), an important molecule of biological origin which can be found in nature, is investigated at the air-water interface using UV- VIS and IR spectroscopy. We employ our newly constructed UV-VIS reflection absorption spectroscopy (RAS) experiment, which is described in detail in this study, along with Infrared reflection absorption spectroscopy (IR-RAS), to probe ATRA at the air-water interface. We elucidate the factors influencing the spectroscopy of ATRA at the air-water interface and compare its spectra at the water surface with results of bulk samples obtained with conventional spectroscopic methods and computational chemistry. Monolayers of pure ATRA as well as mixed ATRA with stearic-d35 acid were prepared and the spectroscopy reveals that ATRA forms J-aggregates with itself, causing a significant redshift of its S0 to S1 electronic transition. Pure ATRA monolayers are found to be unstable at the air-water interface and are lost from
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Article Title: Kinetic Study of Gas-Phase Reactions of Pyruvic Acid with HO2
Authors: J.R. Church, Veronica Vaida, and Rex Skodje
Keywords: Pyruvic acid, quantum chemistry, kinetic rate
Abstract: Gas-phase reactions between pyruvic acid (PA) and HO2 radicals were examined using ab initio quantum chemistry and transition state theory. The rate coefficients were determined over a temperature range of 200–400 K including tunneling contributions. Six potential reaction pathways were identified. The two hydrogen abstraction reactions yielding the H2O2 product were found to have high barriers. The HO2 radical was also found to have a catalytic effect on the intramolecular hydrogen transfer reactions occurring by three distinct routes. These hydrogen-shift reactions are very interesting mechanistically although they are highly endothermic. The only reaction that contributes significantly to the consumption of PA is a multistep pathway involving a peroxy-radical intermediate, PA + HO2 ? CH3COOH + OH + CO2. This exothermic process has potential atmospheric relevance because it produces an OH radical as a product. Atmospheric models currently have difficulty predicting accurate OH concen
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Article Title: Peptide synthesis in aqueous microdroplets
Authors: Veronica Vaida, Alexandra Deal
Keywords: microdoplets, peptides, surface reactions
Abstract: Organic chemistry on water has been shown to occur with large changes in reaction rates, products, and mechanisms as compared with the associated bulk aqueous chemistry (1–8). Chemistry “on” water refers to chemistry occurring between water and any nonpolar media such as oil or air. While detailed mechanisms of chemistry on water are still controversial (1, 9–15), investigations of the structure, charges, and hydrogen bonding at the water surface attempt to elucidate the unique nature of water–air inter- faces, which have been proposed to be auspicious environ- ments for organic reactions (1, 16–19). Holden et al. (2) make a significant contribution in this field, with the syn- thesis of peptides at the surface of microdroplets.
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I certify that the information in the report is complete and accurate:
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Signature Date: 1/17/23 1:34PM

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Scientific Report and Accomplishments

i. Abstract

Atmospheric chemistry occurs in many phases and at interfaces. The project "Atmospheric Aerosols as Chemical Micro Reactors in the Environment" investigated the multiphase chemistry of organic compounds to provide mechanisms for reactions in the gas phase, aqueous phase, and at interfaces important in the natural environment. Emphasis is on processes that increase the chemical complexity of the natural system. The study involved laboratory experiments, simulation chamber studies and chemical theory to look at organic acids, specifically at oxo and hydroxy acids, and provide the database needed to understand their environmental fate. The results of this project pointed to the effect of the structure and configuration of the molecules studied, the effect of O_2, pH, H_2O and sunlight on their environmental fate.

A major discovery was the special chemical role of surfaces and interfaces, specifically the water-air interface present on atmospheric aerosols, fogs, clouds and at the ocean surface. Techniques, such as surface reflection spectroscopy were developed to aid the study of chemistry at the water surface and allowed investigation of morphological and chemical properties of organic films on aqueous solutions.

The water surface on aqueous drops and at the sea surface provides a special and unique reaction environment with qualitatively different thermodynamic and kinetic properties from bulk aqueous solutions. Chemistry initiated at the water surface was found to lead to the synthesis of oligomers increasing the chemical complexity of the system. Solar radiation is the largest source of energy on both the contemporary and early Earth. Multiphase photochemical mechanisms were obtained in which α-keto acids react in aqueous environments to form organic radicals, which then recombine to form larger, more complex lipids. The relevance of this chemistry to reactions in the contemporary atmosphere is to suggest abiotic pathways by which complex molecules and self-assembled particles are generated and contribute to atmospheric chemistry, transport and consequently affect climate.

This interdisciplinary project provided many opportunities for education and outreach to a group of diverse undergraduate and graduate students, postdoctoral fellows and visitors, including international collaborators. Work at the interface of physical chemistry and environmental science was carried out with complementary experimental and computational methods. Students in the group were trained in these complementary approaches. International interactions occurred in collaboration with and participation of researchers in the CESAM group, LISA, Universitè de Paris-Est, University of Copenhagen and Aarhus University in Denmark provided an international context for young researchers involved in this project.

ii. Objectives for the project

The multiphase chemistry of organic compounds is investigated to provide mechanisms for reactions in the gas phase, aqueous phase, and at interfaces important in the natural environment. Emphasis is on processes that increase the chemical complexity of the natural system.

1) Examine the fundamental chemistry photochemistry relevant to environmental systems. Chemical and sunlight-initiated radical reactions are followed in mechanistic detail.

   (a) Development of techniques needed for the study of multiphase reactions started in the first year and continued for the period of the grant.
   (b) Study the multiphase chemistry and photochemistry of organic acids (hydroxy acids and keto-acids) as a function of composition, pH, oxygen and radiation.
   (c) Study the role of the water-air interface in promoting reactions which increases the chemical complexity of the natural system compared with gas or aqueous bulk. Years 1 and 2 investigated chemistry in the bulk phases with years 3-5 identifying and investigating the role of water-air interfaces and geophysical surfaces.

2) Perform environmental simulation chamber studies to test the interplay between different fundamental processes in multiphase reactions. Years 2 and 3 involved experiments at CESAM, LISA, Universitè Paris-Est where fundamental processes investigated in the lab were studied under controlled atmospheric conditions. Data analysis of these studies were performed in years 3-5 and compared the laboratory data to evaluate reactivity of organic acids in the atmosphere in different phases.

3) Perform theoretical and model studies to assess the relative importance of heterogeneous effects and organic radical reactions compared to known chemistry.
   (a) Computational studies to predict structure and spectra of gas phase species studied to aid assignments of experimental spectra (years 1-3)
   (b) Computational studies of the role of water on the structure and chemistry of hydroxy and keto acids using water clusters with these species (years 3-5).
   (c) Assess the magnitude of surface effects to determine their impact in atmospheric models.

iii. Findings

Objective 1: Examine the fundamental chemistry/photochemistry relevant to environmental systems.

(a) Instrument development

Methods were developed for the study of spectroscopy of gas phase species with low vapor pressure such as lactic and pyruvic acids. A major accomplishment was the generation of gas phase lactic acid as well as 2-oxooctanoic acid who previously were not accessible in gas phase. Gas phase vibrational spectra and photochemical reaction products could be obtained using these methods. The first two years also involved the development of methods for the study of solution phase processes for organic acid surfactants with low solubility in water. Particularly challenging was the study of IR spectra in aqueous solutions given interference from vibrational features in water. ATR allowed obtaining vibrational spectra in bulk aqueous solution.

Unique to this project was the development of surface sensitive spectroscopic and photochemical methods in years 3-5. Major accomplishments were the design, building and utilization of surface reflection IR spectroscopy with polarized light and variable incidence angle which allowed obtaining the surface partitioning, morphology and orientation of hydroxy and keto acids as a function of their structure, i.e. nonpolar hydrocarbon tail lengths. Another major accomplishment was the design and implementation of surface reflection UV accomplished in year 5. The electronic spectra and structure of organic acids were monitored at the water-air interface with this newly developed surface reflection UV spectrometer.

Surfaces are difficult to study in part because of the very small number of molecules at the surface. To overcome this difficulty a Blodgett attachment was attached to the Langmuir trough for collecting molecules at the water surface separately from the bulk aqueous phase. Photochemical experiments required illumination of a large area of the Langmuir trough. A major accomplishment was the design and construction using UV LEDs of a photochemical light source which matched the profile of the Langmuir trough allowing efficient photolysis of surface species. The spectroscopic and photochemical surface sensitive methods developed enabled the proposed experiments by increasing the sensitivity for surface species.

(b) The multiphase chemistry and photochemistry of organic acids (hydroxy acids and keto-acids) as a function of composition, pH, oxygen and radiation.

This research found that the chemistry of carbonyl compounds varies with their structure, the presence of O_2 and pH. Reaction rates and mechanisms were investigated for pH 2 to 10 in aerobic and anaerobic conditions for hydroxyacids and oxo acids of different tail lengths. A major accomplishment was quantifying the concentration of the keto, diol, protonated and deprotonated forms as a function of pH.

"pH Dependence of the Aqueous Photochemistry of α-Keto Acids" Rebecca J. Rapf, Michael R. Dooley, Keaten Kappers, Russell J. Perkins, Veronica Vaida *J. Phys. Chem A* **121**, 8368-8379 (2017)

The study of the reaction mechanisms led us to a collaboration with Dr. Thogersen (Aarhus, Denmark) to investigate the primary steps in the light initiated chemistry of lactate. A major accomplishment was that decarboxylation but not dehydration occurs in aqueous solution.

“The primary photo-dynamics of lactate in aqueous solution: decarboxylation prevents dehydroxylation“ Thogersen, Jan, Vaida Veronica, Bregnhoj Mikkel, Weidener Tobias, Jensen Frank *Physical Chemistry Chemical Physics*, **23**(8) 4555-4568 (2021),

A major accomplishment was the photochemical synthesis of lipids initiated by oxoacids even when they reacted with nonabsorbing partners. In the natural environment this chemistry would lead to building complexity of the system.

“Environmental Processing of Lipids Driven by Aqueous Photochemistry of α-Keto Acids” Rebecca J. Rapf, Russell J. Perkins, Michael R. Dooley, Jay A. Kroll, Barry K. Carpenter, Veronica Vaida *ACS Cent. Sci.* **4**(5), 624-630 (2018)

(c) Study the role of the water-air interface

Based on the studies in year 1 and 2, it became obvious that surfaces and interfaces could contribute chemistry not observed in the bulk. Surface sensitive techniques developed in years 3-5 and used to measure the surface partitioning, morphology and orientation of hydroxy and oxo acids as well as their dark and light initiated surface reactions. A major accomplishment was obtaining reaction products and mechanisms for oxoacids at the water surface.

“Water-Air Interfaces as Environments to Address the Water Paradox in Prebiotic Chemistry: A Physical Chemistry Perspective” Deal A.M., Rapf R.J., Vaida V. *J. Phys. Chem. A* **125**(23), 4929-4942 (2021)

“Lactic acid photochemistry following excitation of S_0 to S_1 at 220 to 250 nm” Deal, A. M.; Frandsen, B. N.; Vaida, V. *J. Phys. Org. Chem.* 2022; e4316

“Infrared Reflection Absorption Spectroscopy of Hydroxyacids at the Water -Air Interface” Alexandra M. Deal; Veronica Vaida. *J. Phys. Chem. A.* 126 (44) , pp.8280-8294 (2022)

Based on these findings, the opportunity presented itself to study the morphology and reactivity at geochemical surfaces in collaboration with Prof. Grassian (UCSD). A major finding was that the surface chemistry of pyruvic acid is sensitive to the presence of water and photons. Reactions with surface hydroxyl radicals yield primarily pyruvate and water which upon irradiation generated oligomers, many of whom were not observed in bulk aqueous phase.

“Chemistry and Photochemistry of Pyruvic Acid Adsorbed on Oxide Surfaces” Alves M. R., Fang Y., Wall K. J., Vaida V., Grassian V.H.J. Phys. Chem A (2019)

“Heterogeneous Interactions between Gas-Phase Pyruvic Acid and Hydroxylated Silica Surfaces: A Combined Experimental and Theoretical Study” Fang, Yuan; Lesnicki, Dominika; Wall, Kristin J.; Gaigeot, Marie-Pierre; Sulpitzi, Marialore; Vaida, Veronica; Grassian, Vicki H. *J. Phys. Chem. A* **123**(5), 983-991 (2019)

Objective 2: Environmental simulation chamber studies of the chemistry of oxoacids

The fundamental processes investigated in the lab in Boulder were studied in CESAM, the environmental simulation chamber in Paris (Universitè Paris-Est) in collaboration with Prof. Jean-Francois Doussin. This 4000liter chamber fitted with a solar simulator allowed multiphase experiments which were performed primarily on pyruvic acid and in a more limited way, on 2-oxo-octanoic acid. Experiments were performed in gas phase, in gas phase at different partial pressures of water vapor and on nebulized microdrops of aqueous solutions of pyruvic acid. The chamber allowed experiments at 1 atm of synthetic air as well as 1 atm of N_2 and therefore were able to probe the effect of O_2 on the photochemistry of pyruvic acid. A major finding was that water, even at low partial pressure, is able to modify the ratio of conformers by hydrogen bonding and therefore strongly affects the pyruvic acid chemistry.

"Conformer-Specific Photolysis of Pyruvic Acid and the effect of Water" Blair, Sandra L., Reed Harris Allison E., Frandsen Benjamin N., Kjaergaard Henrik G., Pangui Eduard., Cazaunau Mathieu, Doussin Jean-Francois, Vaida Veronica *J. Phys. Chem A,* **124(**7), 1240-1252 (2020)

Another major finding from the comparison of laboratory and simulation chamber studies was the important role of the water-air interface of the microdroplets produced in the simulation chamber. Zymonic acid was identified as one of the products produced at the water surface but not seen in the bulk.

"Chemistry and Photochemistry of Pyruvic Acid at the Air-Water Interface" Keaten J. Kappes, Alexandra M. Deal, Malte F. Jespersen, Sandra L. Blair, Jean-Francois Doussin, Mathieu Cazaunau, Edouard Pangui, Brianna N. Hopper, Matthew S. Johnson, Veronica Vaida *J. Phys. Chem. A* **125**(4), 1036-1049 (2021)

Simulation chamber studies were inspired by fundamental laboratory results and in turn, suggested further laboratory studies where more detailed mechanistic information of the multiphase chemistry pf pyruvic acid could be obtained.

Objective 3: Theoretical and model studies to assess the relative importance of heterogeneous effects in environmental chemistry.

Theory and computation were important in assessing the importance of conformers of hydroxy and oxoacids that would be present in different phases present in the natural environment. These studies further allowed theoretically predicting spectra and aided assignments of experimentally obtained IR spectra.

"Infrared Spectroscopy of 2-Oxo-Octanoic Acid in Multiple Phases" Kappes, K; Frandsen, B. N.; Vaida, V. *Phys. Chem. Chem. Phys*. **24**, 6757-6768 (2022)

A major finding which rested on theory was that water affects hydrogen bonding in the organic acids studied and modifies their conformer configuration and consequently their chemistry. The competition between intramolecular and intermolecular hydrogen bonding was found to be an important factor in the light initiated chemistry of pyruvic and that of lactic acid.

"Lactic Acid Spectroscopy: Intra and Intermolecular Interactions" Frandsen, Benjamin N., Deal Alexandra M., Lane Joseph R., Vaida Veronica *J. Phys. Chem. A* **125**(1), 281-229 (2021).

Computational studies allowed a careful look at the reaction rates and mechanisms for pyruvic acid reactions with OH and HO_2 which also occur in the atmosphere. These mechanistic studies also accounted for the hydrogen bonding of radicals to pyruvic acid and evaluated the atmospheric reactivity of OH and HO_2 reactions of pyruvic acid in atmospheric conditions.

"Kinetic Study of Gas-Phase Reactions of Pyruvic Acid with HO_2" Church J. R. , Vaida V., Skodje R. T. *J. Phys. Chem A* **125**(11) 2232-2242 (2021)

The main finding from these studies was that sunlight initiated reactions dominate and determine the fate of pyruvic acid in the atmosphere rather than reaction with OH or HO_2.

The quantitative effect of chemistry at the water-air interface could not be calculated but our studies suggest that rates and products can be very different at the water-air interface of both bodies of water and of aqueous aerosols.