Collaborative Research: Detailed Chemical Kinetic Modeling of the Homogeneous Chemical Nucleation of Multicomponent Nanoparticles

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The objective of this project was two-fold: (1) to build a bridge between the US and Belgium by way of collaborative research while enriching the education of one US PhD student and (2) to develop detailed kinetic models of silicon hydride nanoparticle chemistry with the aim of understanding the routes to detrimental particles that form during semiconductor processing and the intentional creation of silicon nanostructures that have interesting electrical and optical properties. A key component of development of these kinetic models is obtaining rate coefficients for each reaction in the mechanism. Quantum chemistry, in particular G3//B3LYP, was used to map the potential energy surfaces of individual reactions in key reaction classes: silylene insertion, hydrogen elimination, and silylene isomerization. Transition state theory was used to calculate rate coefficients, and from these values, a transition state group additivity (TSGA) scheme was used that can estimate activation energies simply based on the structure of the reactant(s). The TSGA scheme holds the promise to replace more approximate kinetic correlations such as the Evans-Polanyi correlation for 'on-the-fly' estimate of reaction barriers during reaction mechanism generation.

INTRODUCTION

Current Award Summary

Particulate contamination is a leading cause of yield loss in semiconductor processing. As integrated circuits become smaller, and as improved cleanroom technology eliminates external sources of particles, homogeneous chemical nucleation of particles within the processing environment is rapidly becoming the most important source of particulate contamination. Fundamental understanding of the chemical nucleation process is essential if we are to control particle formation. This same understanding can help us design methods for aerosol synthesis of nanoparticles and nanostructured materials that are the building blocks of nanoscale science and engineering.

In the current project, we are developing mechanistic models of chemical nucleation of silicon hydrides at Northwestern University in collaboration with Professor Mark Swihart at the University at Buffalo, who is conducting experimental studies of silicon nanoparticle growth and building aerosol models. We are focusing on using automated mechanism generation techniques to create detailed mechanistic models of the early stages of nanoparticle growth that inform the aerosol models by identifying the dominant reaction pathways. Quantum chemical calculations are being used to elucidate reaction channels for silicon hydrides and to develop methods based on group additivity to predict their thermochemical properties.

International Cooperation Summary

The IREE award was used to fund the PhD student working on this project, Andrew Adamczyk, for six months (March to August 2008) at the Laboratorium voor Petrochemische Techniek at Ghent University in Belgium working with Professor Guy Marin, Professor Marie-Françoise Reyniers, and their students. The Marin and Reyniers group offers two areas of expertise that were important for the success of this project. First, they are experts in calculating the contributions of anharmonic corrections to the properties of molecules using quantum chemistry. All thermochemical properties that we calculated prior to the start of the IREE award for silicon hydrides were within the rigid rotor, harmonic oscillator approximation, and we needed to include anharmonicities such as hindered rotation and ring motions including inversion and pseudorotation. Second, Marin, Reyniers and co-workers have developed a novel method for estimating properties of transition states in reactions of hydrocarbons based on a group additivity approach. The IREE collaboration explored the potential of translating this approach to the chemistry of silicon hydrides. This method would offer a new way to estimate the kinetics of reactions of silicon hydrides in the gas phase and simplify the creation of detailed mechanistic models.

The IREE award significantly expanded the intellectual and cultural horizons of the PhD student who spent time in the Marin laboratory. Prior to the IREE award, Andrew Adamczyk spent his entire educational career in the Chicago area, with an undergraduate degree from IIT, work experience at Chicago-based UOP and other corporate centers, and graduate studies at Northwestern. He was very eager to have an opportunity to spend time in an international research setting to gain a better global perspective, experience a new culture, and develop an appreciation for the global marketplace. The Marin laboratory has extremely strong ties to industrial partners all over the world, so Andrew was enlightened by his exposure to the Marin mode of academic/industrial collaboration. He also benefitted by having the opportunity to work in one of the world's leading laboratories for computational kinetics research that has the expertise that was perfectly suited to the advancement of his project. Furthermore, the IREE experience has developed and strengthened the ties between the Broadbelt and Marin groups and led to additional collaboration in the long term. While the two groups have long shared common research interests, they have not carried out any collaborative work prior to the beginning of the IREE award. Most notably, the IREE experience was so successful that Professors Marin and Reyniers offered Andrew Adamczyk the opportunity to stay for an additional year to continue the collaboration.

Research Activities and Accomplishments of the International Cooperation

Upon arrival in Belgium, Andrew immediately created a detailed research program that incorporated both the Broadbelt and Marin laboratories interests. This program focused on validating the TSGA method for silane chemistry while potentially expanding the scope of the current NSF award. Three major reaction families for silicon nanoparticle formation were studied using quantum chemistry: silylene/silene isomerization, silylene elimination/insertion, and hydrogen elimination/insertion. Over 100 different reactions were studied. The quantum chemical analysis of each reaction at the G3//B3LYP level of theory involved several steps: first optimizing the geometries of the product(s) and reactant(s), searching for a valid transition state, and finally optimizing the geometry of that transition state. Once these calculations are completed, transition state theory was applied to calculate rate constants and activation barriers.

Previously, the Evans-Polanyi relationship was used to specify activation energies of reactions based on the heat of reaction. The TSGA method still provides 'on-the-fly' calculation of activation energies during automated mechanism generation but with a higher degree of detail. The validation of TSGA was successfully performed for all three reaction families and will be extended to a fourth in the future (ring opening/closure). Figure 1 shows a comparison of the TSGA method for two major reaction families and the Evans-Polanyi correlations. For all three reaction families studied, the mean absolute deviation of predicted activation barriers for reactions not used in the regression of the group values was less than 2 kcal/mol. Manuscripts summarizing these results are currently in preparation. Evaluation of the TSGA method for pre-exponential factors is in progress.

Anharmonic corrections for hindered rotations were initially deemed necessary for the calculation of rate constants; however, based upon further discussion with the Marin group and preliminary calculations, it was ultimately decided to exclude the correction from the current results. Nevertheless, this still is an interesting area of study. Silicon hydrides form extensive stabilization of lone electron pairs that impede internal rotation favoring the formation hydrogen-bridged intermediates. These intermediates show a filling of the empty p orbital on the silylene center with any nearby hydrogen atom and warrant further research.

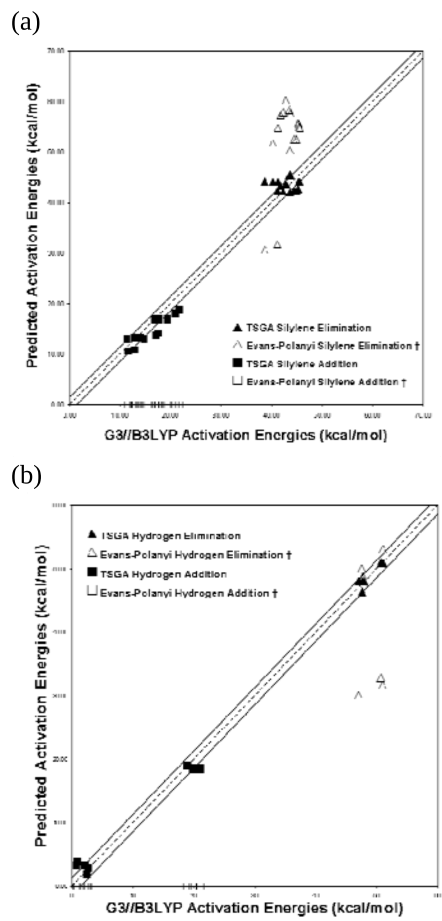

Figure 1: Parity plots of validation of TSGA method and current literature values[1] for the Evans-Polanyi correlation against G3//B3LYP data for two reaction families: (a) silylene insertion/elimination and (b) hydrogen elimination/addition. Solid lines represent error bands giving no more than a factor 2 change in the rate constant. Dashed lines represent perfect parity. Dagger denotes literature values were used in prediction.

Andrew's interaction with the Marin group was facilitated by the submission of a detailed monthly progress report to Professors Broadbelt, Marin, and Reyniers in addition to monthly scheduled meetings with Professor Broadbelt through videoconference.

BROADER IMPACTS OF THE INTERNATIONAL COOPERATION

Expansion of Original Project Scope and Guest/Host Relationship

At this time, Andrew is still working abroad in Belgium. He was offered and accepted a fellowship by the University of Ghent that would extend his stay to August 2009. During this time, Andrew will continue to write the proposed papers on the application of TSGA to predict rate constants. The original project scope was expanded to include a new reaction family (ring opening/closure) and hindered rotation in silylenic species (silicon hydrides with a lone electron pair) will also be explored.

The IREE project has also opened the door for further significant collaborations between the Broadbelt group and the Marin laboratory. Andrew's visit to the Marin laboratory has paved the way for future students in the Broadbelt group as well as other researchers in the US. Notably, he was the first American to study in the Laboratorium voor Petrochemische Techniek. This provided researchers on both sides the chance to see and appreciate cultural differences between the two countries.

Geographic and Cultural Diversity Impacts

Working abroad, Andrew also took advantage of other opportunities that he would not have experienced had he been situated in Chicago. Located in the heart of Europe near Brussels, Belgium, Andrew was able to make connections with a broad range of researchers in Europe and in Asia. For instance, he participated in Eurokin (European Consortium on Chemical Reaction Kinetics) 2008 in Lyon, France. He was also able to attend ChemCon 2008 (in partnership with the Indo-US Symposium on Energy and Sustainability) in Chandigarh, India, to present his work on TSGA to an even broader audience. During his visit, he noted that quantum chemical calculations in the developing country of India are still used infrequently. The eagerness of Indian researchers to learn about the topic and the face-to-face contact have the potential to catalyze new collaborations.

During his stay in Belgium, a trilingual country, Andrew was able to exercise his budding knowledge of the Dutch language while learning basic communication skills in French within and outside the laboratory. To his surprise, he was even able to practice his existing Spanish and Lithuanian language knowledge that he learned in high school and at home, respectively. Since the inception of the European Union and lack of a consolidated language, a multilingual mindset is absolutely necessary to succeed in Europe at any level. Andrew has successfully used the IREE award, in research and more broadly, to understand the importance of clear communication in the dissemination of technical and non-technical information.

Showing his willingness to assimilate to a new culture, Andrew has abandoned his dependence on motor transportation and embraced the Belgian love of biking as he now bikes to the laboratory for a total of 11 km (or nearly 7 miles) per day. This detail shows clearly that the new cultural environment has affected Andrew in a positive way. Andrew anticipates that his experience will be able to impact others upon his return to the US when he presents his findings and shares his experiences with incoming Northwestern University graduate students.

DISCUSSION AND SUMMARY

The 2007-2008 IREE award has been a tremendous success. In detail, the accomplishments of the Broadbelt and Marin research groups are highlighted below:

Intellectual Merit

- The transition state group additivity (TSGA) method has been validated for silicon hydride chemistry. Three to four papers are in preparation related to transition state group additivity for the prediction of rate constants. One for each of the reaction families will be prepared (silylene/silene isomerization, silylene elimination/insertion, hydrogen elimination/insertion, and ring opening/closure).

- An additional paper concerning the presence of extensive lone electron pair stabilization in silylenic species during the course of hindered rotation analysis has been proposed and will be pursued. We propose that this will be done in partnership with the Waroquier group of the Center for Molecular Modeling at the University of Ghent.

Broader Impacts

- The original research collaboration has been extended by 12 months allowing Andrew to stay until August 2009. This has proven that the IREE award is a successful catalyst in forging international research relations.
- Andrew's international perspective has indelibly changed as a result of his stay in Europe. He has been exposed firsthand to the global research landscape. He has shown competence in technical and non-technical problem solving in a new cultural environment, strengthening his position as a scientist in the research community. Finally, the experience abroad has given this early career researcher the opportunity to feel and show independence in his field of research.

To conclude, the reader can find below general suggestions concerning improvements that can be made to the IREE collaborative experience:

- An on-line forum would be helpful for researchers to facilitate communication abroad in addition to pre- and post trip conferences. This forum can be a means of communicating cultural and research experiences real time with other IREE participants and within individual research group collaborations.

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REFERENCES

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BRIEF BIOGRAPHIES OF RESEARCHERS

Linda Broadbelt is Professor in the Department of Chemical and Biological Engineering at Northwestern University. She received her B.S. in chemical engineering from The Ohio State University and graduated summa cum laude. She completed her Ph.D. in chemical engineering at the University of Delaware where she was a Du Pont Teaching Fellow in Engineering. At Northwestern, she was appointed the Donald and June Brewer Junior Professor from 1994-1996. Her research and teaching interests are in the areas of multiscale modeling, complex kinetics modeling, environmental catalysis, novel biochemical pathways, and polymerization/depolymerization kinetics. She is Associate Editor for Energy and Fuels and was the chair of programming for the Division of Catalysis and Reaction Engineering of AIChE from 2003-2008. She was also appointed to the Scientific Organizing Committee for the 19th and 21st International Symposia on Chemical Reaction Engineering and served on the Science Advisory Committee of the Gulf Coast Hazardous Substance Research Center from 1998-2005. Her honors include selection as a Fellow of the American Association for the Advancement of Science, a

Fulbright Distinguished Scholar Award, a CAREER Award from the National Science Foundation, appointment to the Defense Science Study Group of the Institute for Defense Analyses, and selection as the Ernest W. Thiele Lecturer at the University of Notre Dame and the Allan P. Colburn Lecturer at the University of Delaware.

Andrew Adamczyk, the 4^{th} year graduate student working abroad on this project from the Department of Chemical and Biological Engineering University at Northwestern University, has substantial experience in chemical kinetics modeling. He has used Gaussian software for nearly three years and has developed expertise in performing the types of calculations required for this project. He holds a B.S. from the Illinois Institute of Technology with high honors and is currently a Fellow of the ARCS Foundation and the Laboratorium voor Petrochemische Techniek at the University of Ghent in Belgium.