THE JOURNAL OF PHYSICAL CHEMISTRY A

 VOLUME 113, NUMBER 42, OCTOBER 22, 2009

Titan: A Strangely Familiar World

With the Cassini/Huygens mission to Saturn and its environs now providing the closest view ever of a distant planetary system, we have learned that the great moon, Titan, is indeed Earth "as seen through a glass, darkly."[1] Titan has long been thought to resemble a frozen primordial version of our home planet, and its atmosphere exhibits remarkable parallels to our own.[2,3] It is dense, 1.4 bar at the surface, primarily nitrogen with a few percent methane and countless trace constituents but little oxygen. With a surface temperature of 90 K, there exists a "methanological cycle" analogous to the hydrological cycle on earth, that gives rise to methane clouds and rain.[4,5] There is a tropopause at 75 K and a stratosphere that is considerably warmer owing to absorption of solar radiation by dense haze layers playing the role of ozone on Earth.[6] This complex haze has completely obscured the surface until the recent infrared and radar imaging from Cassini, the more limited terrestrial observations in the infrared, and the visible imaging directly from the surface by the Huygens probe. The parallels to Earth's atmosphere have been known or suspected since Voyager missions in the 1970s, but our growing knowledge has now deepened this sense of a cold, haze-enshrouded *Doppelgänger*. There is a diverse surface geology including cryovulcanism and "sand" dunes but the nature of the "sand" is unclear: it could be water ice particles or hydrocarbon/nitrile tars from haze precipitation.[7] There are methane/ethane lakes[8] and evidence of river channels etched deeply into the surface.[9] There are well-defined seasons and seasonal weather.[10] From these dark reflections of our own world we can hope to gain insight into our own history and into both the universal themes and notable exceptions in planetary atmospheres, their formation and chemical evolution.

In addition to the remarkable images provided by the Cassini/Huygens mission, a wide range of detailed measurements have been made, providing deep new insight into the rich chemistry of its atmosphere.[11−14] These measurements arrive coincident with the emergence of a new approach to laboratory investigation of astrochemical problems, what may be termed *Astrochemical Dynamics*. Until recently, astrochemical laboratory measurements have largely been spectroscopic in nature, more or less in support of astronomical observation. In the case of Titan's haze, there have also been various direct experimental simulations of the atmosphere.[15] As more concrete chemical information has emerged, the effort to model Titan's atmosphere has developed in parallel.[2,3,16,17] These models encompass large networks of elementary reactions in which rate constants are often, out of necessity, guessed or extrapolated from temperatures higher than those relevant to the system under study. Just as fundamental studies of elementary reactions have transformed the study of combustion chemistry, applications of powerful methods to probe reactive or photochemical events under single-collision conditions,[18−20] and to record reaction kinetics at the relevant temperatures,[21−23] are now being applied to astrochemical problems to guide the modeling studies as well as the observations. The goal now is to understand the *chemical dynamics* of these environments, not just their chemical composition. These developments may be traced to molecular beam photochemistry by Jackson and others,[24,25] to low-temperature kinetics measurements by Sims, Smith, and Rowe,[21−23] to crossed-beam reactive scattering applications from Kaiser and co-workers,[26−28] and to kinetics and dynamics studies from the Leone[29] and Zwier[30] goups. All of these studies have benefitted from the advent of powerful ab initio calculations to guide and help interpret the experiments. Ongoing advances have followed from many groups around the world as the suitability of these approaches to probe the chemistry of these extreme environments has become clear.[31−33]

This convergence of fundamental dynamics investigations, ab initio theory, low-temperature kinetics measurements and modeling, together with the anticipated results from the Cassini/Huygens mission, led Ralf Kaiser (University of Hawaii), Alex Mebel (Florida International University), Ian Sims (University of Rennes), and me to develop an NSF Collaborative Research in Chemistry (CRC) network in 2006 focused on the fundamental chemistry underlying the formation and growth of Titan haze aerosols. In February, 2009, the third in a series of annual workshops, "Titan Chemistry: Observations, Experiments, Theory and Modeling" was held in San Juan, PR, as an outgrowth of this CRC network. The goal of these workshops has been to bring together those engaged in fundamental reaction dynamics, kinetics and ab initio investigations, with modelers and with scientists associated with the Cassini mission or with Earth-based observations, to gain deeper insight into Titan's complex chemistry. The workshop featured lectures ranging from an overview of the formation and evolution of Titan's atmosphere, to results from Cassini ionospheric chemistry, from laboratory simulations of haze components to crossed-beam scattering of haze building blocks, from hydrocarbon photochemistry to cosmic ray impacts on ices, and from an overview of past and current space missions to future proposals for Titan exploration. A key feature of the workshop was to bring together those focused on ion chemistry with those studying neutral reactions.

10.1021/jp908522j CCC: $40.75
Published on Web 10/15/2009

This special section of *The Journal of Physical Chemistry A* embodies papers arising from presentations at the Workshop, as well as others from those unable to attend. Rather than summarize the papers themselves, which are readily available in the accompanying pages, I will just highlight some of the questions they raise and attempt to answer to pique the reader's interest: What are the primary ionic species responsible for formation of benzene cations on exposure of Titan's atmosphere to extreme ultraviolet radiation? What are the electronic absorption spectra of extended polyynes, and how do they vary with carbon chain length? Can exposure of Titan haze analogs to soft X-ray radiation give rise to biologically relevant molecules? What is the structure of pure hydrocarbon aerosols potentially formed in Titan's atmosphere? What are the products and branching for UV photodissociation of cyanoacetylene? What are the underlying dynamics for reaction of ethynyl radicals with ethylene, and what are the primary products? What is the physical state of water ice on Titan? What are the dynamics and primary products of the reaction of ethyl cation with benzene? What can we learn of the history of Titan's atmosphere from the $^{13}C/^{12}C$ ratio in ethane? What are primary products and the underlying mechanisms in the reaction of excited nitrogen atoms with methane? Is there a potential role for doubly ionized species in Titan's atmosphere? Can we understand the total carbon budget in Titan's atmosphere, and what can this tell us of the history of its atmosphere? How do room temperature reaction rates relate to those at conditions relevant to Titan for key reactions? These and many other questions are treated in the rich and diverse assembly of papers in the following pages.

Acknowledgment. I acknowledge the National Science Foundation for support of this research under grant number CHE-0627854. I thank the Office of the Vice President for Research and the Chemistry Department at Wayne State University, as well as Newport/Spectra-Physics lasers, for support of the workshop. I am also grateful to Prof. George Schatz, Prof. Tim Zwier, and Dr. Donna Minton for their support and assistance in preparing this special section on Titan's Chemistry. Finally, I acknowledge all the workshop participants and authors of the papers in this volume for their stimulating contributions.

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JP908522J