

Physical Chemistry Seminar

Tuesday,
October 1, 2013

11:00 am

Room 1315
Chemistry Building

Following Isomer-resolved Chemical Pathways in Atmospheric and Combustion Chemistry



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Host: Professor Etienne Garand

The determination of the rates of chemical reactions and the products they produce plays an important role in understanding complex chemical environments, such as those encountered in combustion and atmospheric chemistry. Chemists usually measure rate coefficients by monitoring the loss of a reactant, but knowledge of product branching ratios is equally important to determining the downstream influence of an elementary reaction in a complex environment. For most reactions, there is even less knowledge about the isomeric identities of each product, despite the fact that different isomers may have vastly different reactivities. In this talk, I will describe our experiments that follow chemical reaction pathways using time-resolved multiplexed photoionization mass spectrometry with isomeric specificity. I will discuss two reaction classes we have studied that directly impact humans and the environment: the initial steps of soot formation in combustion, and the oxidation of alkenes via ozone in earth's atmosphere. There is mounting evidence that the rate limiting step in soot formation chemistry is the formation of the first and second aromatic rings in the combustion of aliphatic fuels. Resonance-stabilized free radicals, most notably the C_3H_3 (propargyl) radical, play key roles in this chemistry due to their enhanced stability. We have studied the reaction of propargyl radicals with acetylene, following branching reaction pathways through C_5H_5 , C_7H_7 , and C_9H_8 intermediates and products. In atmospheric chemistry, the oxidation of alkenes (emitted in vast quantities by plants) via ozone has been postulated for 60 years to proceed via a "Criegee" intermediate. We have made the first detection of Criegee intermediates in the gas phase, and have studied their reactivity with atmospherically relevant molecules. Our directly measured rate coefficients are dramatically different than values used in some atmospheric models. In addition, we observe conformer-specific reaction rates for acetaldehyde oxide, highlighting the value of isomer-resolved detection schemes in unraveling chemical reaction mechanisms. I will discuss the implications that direct monitoring of Criegee intermediates may bring to our understanding of atmospheric oxidation pathways.

Refreshments will be available prior to the seminar at 10:45 a.m. outside room 1315

Graduate Students may meet with the speaker at 1:00 p.m. in Room 8335