CHEMISTRY SEMINAR

Dr. Richard P. Johnson
Department of Chemistry, University of New Hampshire

Tuesday, October 2, 2018, 1:00 – 1:50 p.m.
Room EN2043 (Engineering Building)

Title: Acid Catalyzed Rearrangements in Arenes: A Multitude of Mechanisms

Abstract:

The acid catalyzed interconversion of substituted aromatic compounds by group migrations (Eq. 1, R = aryl or alkyl) is believed to occur through the intermediacy of ipso arenium ions, which result from protonation at sites bearing substituents.¹ Skeletal rearrangements of polycyclic arenes can also be acid catalyzed, as first shown by Dansi and Salvioni in 1941.² Only scattered literature exists on this topic since that time. We have studied acid catalyzed skeletal rearrangements in naphthalene, anthracene and tetracene isomers using both experiment and DFT computations. Experimental studies are carried out in a microwave reactor which provides a safe method for studying elevated temperature superacid chemistry.

For naphthalene, no skeletal rearrangement is observed; this is consistent with earlier studies³ and our high predicted barrier to isomerization. Unidirectional rearrangement of anthracene to phenanthrene is observed; both experiment and computations support a complex mechanism, suggested earlier⁴ which passes through tetrahydroanthracene. For the four-ring acene series shown above, interconversion among isomers (Eq. 2) favors chrysene at equilibrium. An aryl pirouette mechanism through spirocyclic intermediates is supported by a detailed mapping of the potential energy surface for cationic.

Work in progress on simple alkyl benzenes (Eq. 3) supports dissociation to π complexes of benzene with classical and nonclassical cationic intermediates in which complex rearrangements can occur.