Research challenges fundamental precept of organic chemistry

July 11 2014, by Alan Flurry

A family of millions of known chemical compounds called "aromatics" or "arenes" and their products, including a great number of medicines, plastics and synthetic fibers, are characterized by their regular arrangement of ring atoms instead of alternating single and double bonds. A new study published by researchers in the University of Georgia Franklin College of Arts and Sciences department of chemistry posits a different fundamental mechanism for the way these compounds react to replace atoms.

The study, "Arenium ions are not obligatory intermediates in electrophilic aromatic substitution," was published June 27 in the early online edition of the *Proceedings of the National Academy of Sciences*.

Benzene, the "aromatic" prototype, was discovered by Michael Faraday in 1825 as a colorless flammable constituent of the then-used illuminating oil. Along with other aromatics such as naphthalene, or mothballs, it also is found in crude oil.

Aromatics constitute a diverse and widely used chemical family. Employed to make derivatives, benzene consistently ranks among the top 20 chemicals produced annually.

The key chemical reaction giving these derivatives depends on the underlying ring structure. "Electrophilic aromatic substitution" describes the reaction whereby an atom of an aromatic is replaced by another of an "electron-seeking" reagent. This fundamental organic chemical reaction

of aromatics is the focus of the paper.

"The electrophile is supposed to attach itself to the aromatic in a first stage to give an 'intermediate,' from which another group, present at the same site, is then lost in a second stage," said Paul von Ragué Schleyer, Graham Perdue Professor of Chemistry at UGA and one of the study's authors. "Although this putative intermediate has garnered much attention in the literature as a simplification, we find instead that it doesn't exist when the reaction conditions are modeled computationally."

The research team found that a fundamentally different pathway is followed, one that harks back to the "addition-elimination mechanism" that was favored for decades before "electrophilic aromatic substitution" became generally accepted in the 1940s.

"We are excited about the new study," said Henry "Fritz" Schaefer, Graham Perdue Professor of Chemistry and director of the Center for Computational Chemistry at UGA. "It will change the way organic chemists think about some of the most fundamental reaction mechanisms in chemistry."

More information: Boris Galabov, Gergana Koleva, Svetlana Simova, Boriana Hadjieva, Henry F. Schaefer III, and Paul von Ragué Schleyer. "Arenium ions are not obligatory intermediates in electrophilic aromatic substitution." *PNAS* 2014 ; published ahead of print June 27, 2014, DOI: 10.1073/pnas.1405065111

Provided by University of Georgia