Department of Chemistry

College of Science & Engineering

University of Minnesota

Seminar

Izaak M. Kolthoff Lectureship in Chemistry #2

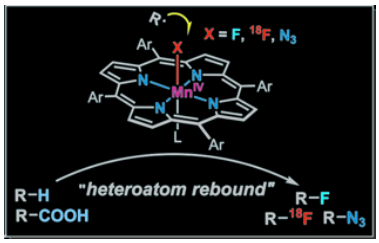
4 p.m.
Wednesday, Sept. 19, 2018
331 Smith Hall

Heteroatom Rebound Catalysis – New Reactivity for High-valent Fe-X and Mn-X Species

Professor John T. Groves

Department of Chemistry, Princeton University

Host: Professor Lawrence Que Jr.



In this lecture, I will discuss recent developments from our lab in the areas of C-H activation and functionalizations mediated by iron and manganese porphyrins and related porphyrazines (1-5). A perspective of the current state of the field will be presented with connections to key conceptual advances regarding the preparation and characterization of high-valent metal-oxo species and their reactivity. We have directly observed and kinetically characterized the reactive iron and manganese intermediates employing *in operando* methods during functional catalysts. Our studies of C-H hydroxylation have led to the discovery of a selective and efficient C-H chlorinations and *fluorinations* mediated by synthetic manganese porphyrins. These protocols have also enabled practical C-H azidations and most recently, a novel C-H isocyanation reaction. The methods allow facile production of fluorinated and nitrogenated building blocks and drug analogs directly from readily available precursors. Further, fluorination with 18F sources have allowed access to new PET imaging agents using high-valent metal fluorides.

1. Xiongyi Huang and John T. Groves, Beyond ferryl-mediated hydroxylation: 40 years of the rebound mechanism and C-H activation, *J. Biol. Inorg. Chem*. **2017**, 22, 185–207.
2. Gang Li, Andrew K. Dilger, Peter T. Cheng, William R. Ewing, John T. Groves, Selective C-H Halogenations with a Fluorinated Manganese Porphyrin, *Angew. Chem*. **201**8, *57*, 1251-1255.
3. Wei Liu, Mu-Jeng Cheng, Robert J. Nielsen, William A. Goddard III, and John T. Groves, Probing the C-O bond-formation step in metalloporphyrin catalyzed C-H oxygenation reactions, *ACS Catalysis*, **2017**, *7*, 4182-4188.
4. Xiongyi Huang, Thompson Zhuang,† Patrick A. Kates, Hongxin Gao, Xinyi Chen, and John T. Groves, Alkyl Isocyanates via Manganese-Catalyzed C-H Activation for the Preparation of Substituted Ureas , *J. Am. Chem. Soc.* **2017**, *139*, 15407-15413.
5. Wei Liu, Xiongyi Huang, Micheal Placzek, Shane W. Krska, Paul McQuade, Jacob M. Hooker, John T. Groves, Site-selective 18F fluorination of unactivated C-H bonds mediated by a manganese porphyrin, *Chem. Sci.*, **2018**, *9*, 1168-1172.

Professor John T. Groves' research program is at the interface of organic, inorganic, and biological chemistry. Current efforts focus on the design of new, biomimetic catalysts and the molecular mechanisms of these processes, the design and assembly of large scale membrane-protein-small molecule constructs, studies of host-pathogen interactions related to iron acquisition by small molecule siderophores, and molecular probes of the role of peroxynitrite in biological systems.

Professor Groves received an undergraduate degree in chemistry at the Massachusetts Institute of Technology, where he worked with Frederick Greene. In 1965, he began his doctoral studies under the direction of Professor Ronald Breslow at Columbia University. Upon receiving his doctorate, Groves began his independent research career at the University of Michigan, in 1969. In 1985, he moved to Princeton University where he is Hugh Stott Taylor Chair of Chemistry. Groves is an award-winning inorganic chemist, receiving numerous accolades, including the American Chemical Society National Award in Inorganic Chemistry and the Sigma-Aldrich Award in Inorganic Chemistry. He is a member of the National Academy of Sciences, the American Academy of Arts and Sciences, and a Fellow of the Royal Society of Chemistry.

Additional information: z.umn.edu/JohnGrovesLecture2

Izaak Maurits Kolthoff was born on February 11, 1894, in Almelo, Holland. He died on March 4, 1993, in St. Paul, MN. In 1911, he entered the University of Utrecht, Holland. He published his first paper on acid titrations in 1915. On the basis of his world-renowned reputation, he was invited to join the faculty of the University of Minnesota's Department of Chemistry in 1927. By the time of his retirement from the University in 1962, he had published approximately 800 papers. He continued to publish approximately 150 more papers until his health failed. His research, covering approximately a dozen areas of chemistry, was recognized by many medals and memberships in learned societies throughout the world, including the National Academy of Sciences and the Nichols Medal of the American Chemical Society. Best known to the general public is his work on synthetic rubber. During World War II, the government established a comprehensive research program at major industrial companies and several universities, including Minnesota. Kolthoff quickly assembled a large research group and made major contributions to the program. Many of Kolthoff's graduate students went on to successful careers in industry and academic life and, in turn, trained many more. In 1982, it was estimated that approximately 1,100 Ph.D. holders could trace their scientific roots to Kolthoff. When the American Chemical Society inaugurated an award for excellence in 1983, he was the first recipient.