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### Education

Ph.D. (October, 1975); Columbia Univ. NY, USA, B.S (June, 1970): Stanford Univ. USA

#### Academic Carrier

1975 (October) - July (1977): Post-doctoral fellow, Department of Chemistry, Cambridge University, England (supervisor: Prof. Jack Lewis)
1977 (September): Assistant Professor, Department of Chemistry,
State University of New York (SUNY) at Albany, Albany, NY, USA
1984 (September): Assistant Professor, Department of Chemistry
State University of New York (SUNY) at Albany, Albany, NY, USA
1987 (September): Professor Department of Chemistry,
State University of New York (SUNY) at Albany, Albany, NY, USA
1987 (September): Professor Department of Chemistry,
State University of New York (SUNY) at Albany, Albany, NY, USA
1990 (April)-: Professor, Dept/ of Chemistry, Johns Hopkins Univ. Baltimore, MD USA
1999-: September, Ira Remsen Chair in Chemistry. Johns Hopkins University
Baltimore, MD USA
2009-: Professor, Department of Bioinspired Science, EWHA Womans University, Seoul, KOREA

#### Awards and Honors

2011 "Maryland Chemist of the Year" AWARD
2009 F. Albert Cotton Award in Synthetic Inorganic Chemistry American Chemical Society (ACS) National Award
2009 ACS Sierra Nevada Distinguished Chemist Award
1992, Elected Fellow, American Association for the Advancement of Science (AAAS)
1991 Buck-Whitney Award (ACS Eastern New York Section Research Award)\

# **Total Publications**

293 Research Paper, 4 Edited Monographs, 1972-2011. Citations (SCI): 11,595 (2011, September), h-index: 60

# **Representative Publications (recent)**

Peterson, R. L.; Himes, R. A.; Kotani, H.; Suenobu, T.; Tian, L.; Siegler, M. A.; Solomon, E. I.; Fukuzumi, S.; Karlin, K. D. "Cupric Superoxo-Mediated Intermolecular C–H Activation Chemistry" *J. Am. Chem. Soc.* **2011**, *133*, 1702-1705.

Halime, Zakaria.; Kotani, Hiroaki; Li, Yuqi; Fukuzumi, Shunichi.; Karlin, Kenneth D. "Homogeneous catalytic  $O_2$  reduction to water by a cytochrome c oxidase model with trapping of intermediates and mechanistic insights" *Proc. Natl. Acad, Sci. USA* **2011**, *108*, 13990-13994.

# Heme-Copper O<sub>2</sub> and •NO Adducts and Chemistry: Bioinorganic Aspects

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There is fundamental interest and importance in both the chemistry and biochemistry concerning the interactions of molecular oxygen and nitrogen oxides with iron and copper centers. Our research aims to contribute to a fundamental understanding of these topics via the examination of synthetically derived model systems.

Model systems for cytochrome c oxidase (heme & Cu) O<sub>2</sub>-binding and reduction are being pursued and dioxygen reactions with reduced (heme)Fe<sup>II</sup>...Cu<sup>I</sup> ensembles lead to peroxobridged Fe<sup>III</sup>-(O<sub>2</sub><sup>2-</sup>)-Cu<sup>II</sup> complexes. These have been characterized by a variety of spectroscopic or physico-chemical approaches. The significant effect of the nature of the copper-ligand on the Fe<sup>III</sup>-(O<sub>2</sub><sup>2-</sup>)-Cu<sup>II</sup> structure, and conversion to low-spin analogues, B-Fe<sup>III</sup>-(O<sub>2</sub><sup>2-</sup>)-Cu<sup>II</sup> (B = imidazole base axial ligand) will be described. Physical properties and reactivity differences between high and low-spin compounds will be discussed, along with initial results concerning O-O bond cleavage in a (B)-Fe<sup>III</sup>-(O<sub>2</sub><sup>2-</sup>)-Cu<sup>II</sup> system.

Nitrogen monoxide (•NO) interactions with certain copper, heme and heme-copper complexes will also be discussed, in the context of O<sub>2</sub>-interactions with these same complexes. Peroxynitrite (O=N-O-O<sup>-</sup>), normally described as the product of superoxide anion plus •NO, forms by reaction of •NO<sub>(g)</sub> with a copper-dioxygen adduct. A heme-dioxygen adduct reacts with •NO<sub>(g)</sub> to give a heme-nitrate (NO<sub>3</sub><sup>-</sup>) product. Evidence supports the intermediacy of a peroxynitrite-heme complex; reference to heme enzymes effecting this reaction will be made. Also, a heme-copper assembly reacts with nitrogen monoxide to effect its reduction to nitrous oxide (2 •NO<sub>(g)</sub> + 2 $e^{-}$  + 2H<sup>+</sup> —> N<sub>2</sub>O<sub>(g)</sub> + H<sub>2</sub>O), a reaction which mimics the chemistry carried out heme/non-heme diiron nitric oxide reductases (NORs) and certain heme/Cu cytochrome *c* oxidases C*c*Os).

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