VOLUME 40 NUMBER 7

ACCOUNTS of CHEMICAL RESEARCH®

JULY 2007

GUEST EDITORIAL

Dioxygen Activation by Metalloenzymes and Models

Dioxygen is essential in life processes, and metalloenzymes activate dioxygen to carry out a variety of biological reactions including biotransformation of naturally occurring molecules, oxidative metabolism of xenobiotics, and oxidative phosphorylation. One primary goal in metalloenzyme research is to understand the structures of active sites and reactive intermediates and the mechanistic details of dioxygen activation and oxygenation reactions occurring at the active sites. Metalloenzymes use diverse active sites to activate dioxygen, such as heme iron sites, mono- and dinuclear nonheme iron sites, mono- and dinuclear copper sites, a heteronuclear heme iron–copper site, and other metal sites. Despite this diversity of active sites, a common mechanistic hypothesis for dioxygen activation is emerging. In this unified scheme, dioxygen first binds to a reduced metal center, metal–superoxo and –peroxo intermediates are then formed, and then O–O bond cleavage of metal–hydroperoxo species occurs to form high-valent metal–oxo oxidants that carry out substrate oxidations. The objective of this special issue is to report recent developments in the research areas of dioxygen–activating metalloenzymes and their models. A number of new reactive intermediates have been characterized or proposed recently, and new mechanistic insights into O–O bond activation have been proposed as well. One notable example is the striking advances in identifying reactive intermediates and understanding their chemical properties in oxidation reactions in non-heme iron enzymes and their model compounds. Thus, it would be very timely to have a special issue focusing on the molecular mechanistic aspects of dioxygen activation and oxygen atom transfer in enzymatic and biomimetic reactions, and this special issue demonstrates the richness of the chemistry associated with dioxygen activation at metal centers.

The idea of having this special issue in *Accounts of Chemical Research* stems from the symposium of "Dioxygen Activation Chemistry of Metalloenzymes and Models" in Pacifichem 2005 that I organized with Professors Shinobu Itoh and Lawrence Que, Jr. Since we, including speakers and audience, enjoyed the symposium very much with fruitful discussion, I contacted Professor Joan S. Valentine, Editor-In-Chief, to propose a special issue dedicated to the topic of "Dioxygen Activation Chemistry". I also contacted some of the speakers in the symposium to ask for their contributions to this issue, and all of them accepted my invitation without a single rejection despite their busy schedules. Thus, as the guest editor, I thank all the authors for their timely and worthy contributions. I also thank Ms. Rhea Rever for her tremendous work during the editorial process. My warmest acknowledgment goes to Professor Joan S. Valentine *not only* for giving me such a great opportunity to organize this special issue *but also* for being a super advisor during my Ph.D. program at UCLA. Finally, I hope that this issue inspires readers to encounter the fascinating dioxygen activation chemistry of metalloenzymes and models and, even more importantly, to participate in the joyful research field that has been continuously developed by bioinorganic chemists.

Wonwoo Nam

Guest Editor
Ewha Womans University, Seoul, Korea

AR700131D

10.1021/ar700131d CCC: $37.00
Published on Web 07/17/2007