

Preface to Volume 15

Sustaining Life on Planet Earth: Metalloenzymes Mastering Dioxygen and Other Chewy Gases

In this volume of the *Metal Ions in Life Sciences* series the mastering of dioxygen (O_2), methane (CH_4), and ammonia (NH_3) by mainly manganese-, iron- and copper-dependent metalloenzymes and their biomimetic complexes is discussed. It is closely related to Volume 14, *The Metal-Driven Biogeochemistry of Gaseous Compounds in the Environment*, which deals with the biogeochemistry of gases including dihydrogen (H_2), carbon monoxide (CO), acetylene ($\text{HC}\equiv\text{CH}$), dinitrogen (N_2), nitrous oxide (N_2O), hydrogen sulfide (H_2S), and dimethylsulfide ($\text{CH}_3\text{-S-CH}_3$). The accumulation of O_2 in the atmosphere forever changed the surface chemistry of the Earth. Dioxygen, as electron acceptor, is used in the respiration of numerous different organisms that conduct a wide variety of chemically complex metabolisms. To produce O_2 , and to conserve energy by activating and transforming O_2 , CH_4 , or NH_3 , sophisticated metal-dependent enzymes had to be evolved by Nature. These catalysts can overcome unusually high activation barriers of kinetically inert molecules, still a tremendous challenge in the chemical laboratory today.

In the first chapter, the reader is shortly introduced to several aspects and properties of this special molecule “dioxygen” and its extraordinary impact on our current Earth. Just think of water (H_2O), perhaps the most important compound containing oxygen, a superb solvent for numerous biomolecules, and the main source of O_2 in the atmosphere. Carl Zimmer reports in his article entitled “The Mystery of Earth’s Oxygen” (The New York Times, October 3, 2013) about the work of the geochemist D. E. Canfield from the University of Southern Denmark: “There’s something astonishing in every breath we take. What is even more astonishing is that the Earth started out with an oxygen-free atmosphere, it took billions of years before there was enough of it to keep animals like us alive”. Clearly, oxygen must be considered one of the most important elements on Earth,

it means life for all aerobes. Eliminate O_2 and they cannot conserve enough energy to support an active lifestyle.

Chapter 2 deals with the light-driven production of dioxygen by photosynthetic organisms. O_2 is abundant in the atmosphere because of its constant regeneration by the photosynthetic oxidation of H_2O . This process is catalyzed by a unique Mn_4CaO_5 cluster located in photosystem II, a gigantic multi-subunit membrane protein complex. Results and interpretations, especially from state-of-the-art X-ray spectroscopy studies, are summarized. These studies focus on the geometric and electronic structure and the changes as the Mn_4CaO_5 site proceeds through the catalytic cycle.

The following Chapter 3 is devoted to O_2 -generating reactions in the dark. These are rare in biology and difficult to mimic synthetically. Recently, perchlorate-respiring bacteria have been discovered which carry a heme-containing chlorite dismutase. Notably, the enzyme bears no structural or sequence relationships with known heme peroxidases or other heme proteins. These microorganisms detoxify chlorite (ClO_2^-), the end product of the perchlorate (ClO_4^-) respiratory pathway, by rapidly converting ClO_2^- to O_2 and chloride (Cl^-).

In Chapter 4 a long time embattled enzyme is reviewed: Cytochrome *c* oxidase, the terminal oxidase of cell respiration. This redox-driven proton pump reduces molecular oxygen to H_2O . Highly resolved three-dimensional structures of the bovine enzyme in various oxidation and ligand binding states have been obtained; they show that the O_2 reduction site – a dinuclear Fe (heme a_3), Cu (Cu_B) center – drives a non-sequential four-electron transfer for complete reduction of O_2 to H_2O without the release of toxic reaction intermediates like the superoxide anion ($O_2^{\bullet -}$), hydrogen peroxide (H_2O_2), or the hydroxyl radical ($OH^\bullet$). X-ray structural and mutational analyses of bovine cytochrome *c* oxidase, which hosts a sophisticated catalytic machinery for efficient proton and electron delivery, reveal three possible proton transfer pathways which can transfer pumped protons and water-forming protons.

Chapter 5 surveys recent important advances in the field of transition metal complexes and the activation of O_2 . Studies of synthetic models of the diverse iron and copper active sites have led to fundamental chemical insights into how O_2 coordinates to mono- and multinuclear Fe and Cu centers and is reduced to superoxo, peroxy, hydroperoxy, and, after O-O bond scission, oxo species relevant to proposed intermediates in catalysis. The involvement of disparate metal ions, nuclearities, geometries, and supporting ligands provides a rich tapestry of reaction pathways by which O_2 is activated.

Chapters 6 and 7 focus on the functionalization of the gases methane (CH_4) and ammonia (NH_3), both in the presence and absence of dioxygen. In view of their fundamental importance, a remarkable set of tools appears to exist in Nature to convert CH_4 and NH_3 . These are inert molecules and complex transition metal-dependent enzymes (methane and ammonia monooxygenases) isolated from aerobic microorganisms and have been reported to break up the N-H and C-H bonds. Two distinct methane monooxygenases, a copper-dependent membrane protein and an iron-dependent cytosolic protein, catalyze the conversion of CH_4 to

methanol (CH_3OH), thus playing a significant role in the biogeochemistry of this potent greenhouse gas. The reaction of the reduced Fe (or Cu) centers with O_2 leads to intermediates that activate the relatively inert C-H bonds of hydrocarbons to yield oxidized products. Notably, there exist “impossible” microorganisms which use the oxidative power of nitric oxide (NO) by forging this molecule to ammonium (NH_4^+), thereby making hydrazine (N_2H_4). Others can disproportionate NO into N_2 and O_2 . This intracellularly produced O_2 enables these “impossible” bacteria to adopt an aerobic mechanism for methane oxidation.

In summary, this volume, like the preceding volume 14 of the *Metal Ions in Life Sciences* series, offers a wealth of profound information about important processes in our current biosphere. The emphasis is on the fundamental role of molecular oxygen for all aerobically living organisms including humans, animals, and plants. The crucial role of transition metals, specifically of manganese, iron, and copper, is addressed in the activation, production, and transformation of molecular oxygen, but also in the functionalization of methane and ammonia and their impact on the environment.

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