

Chemistry Congress: 2018 Oxidation chemistry of group 10 metal diphenoxide complexes- Yuichi Shimazaki

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Chemistry of redox active transition metal complexes with pro-radical ligands and their detailed electronic structures have been actively pursued in recent years. An “experimental” valence state in metal complexes is sometime different from the “formal” oxidation state, especially in the species having redox active ligands. This difference can be also seen in biological system, such as iron(IV)-porphyrin p-cation radical in some heme proteins and copper(II)-phenoxyl radical in galactose oxidase (GO). Many efforts for determination of the experimental oxidation number have been close to the goal of the “truth oxidation state” in various oxidized metal complexes with redox-active ligands. Depending on the relative energies of the redoxactive orbitals, metal complexes with the redox active ligands exist in two limiting descriptions, either a metal-ligand radical ($M^{n+}(L^{\bullet})$) or a high valent metal ($M^{(n+1)+}(L^-)$) complex. The reaction mechanisms of artificial and biological catalysts depend on the electronic structures of the high valent intermediates. However, geometric and electronic structural characterizations of the high valent species have been rare due to their stability. Recently, some artificial metal-phenoxyl radical complexes as models of GO have been synthesized and successfully characterized by X-ray crystal structure. The one-electron oxidized metal-phenolate complexes showed various electronic structures depending on small perturbations, such as substitution of the phenolate ring and the chelate effect of the phenolate ligands and so on. In this presentation, I will focus on X-ray crystal structures of the one and two-electron oxidized metal(II)-phenolate complexes (Ni(II), Pd(II), Pt(II) and Cu(II)) with Schiff base ligands of 2N2O donor sets. Especially electronic and geometric structure relationship such as differences of metal-phenoxyl radical and highvalent metal phenolate complexes, and the effect of different oxidation locus of the radical electron on the ligands in oxidized forms will be discussed.

Oxidation is the reaction of a molecule, an atom, or an ion during a loss of electrons. When the oxidation occurs, the molecule of the state of the oxidation, the

atom or ion, is increased. The reverse process is called reduction, which occurs when an electron gain or an atom of the state of the oxidation decreases. The oxidation in which oxygen is involved is always the term of the modern definition of oxidation. However, there is another old definition of hydrogen that can be found in organic chemistry texts. This is the opposite of the definition of oxygen, so it can be confusing. It is still good to be aware.

An ancient meaning of oxidation when added to a compound. Indeed, gaseous oxygen (O_2) was the first known oxidizing agent. While adding oxygen to a compound often meets the criteria for losing electrons and increasing the state of oxidation, the definition of oxidation has expanded to include.

Electrochemical reactions are excellent examples of oxidation reactions. When a copper wire is placed in a solution containing silver ions, electrons are transferred from metallic copper to silver ions. Metallic copper is oxidized. Silver metal whiskers grow on the copper wire while the copper ions are released into the solution.

Once the electron has been told and the reactions). A type of chemical reaction in which oxidation and reduction occur is called a redox reaction, which means reduction-oxidation. The oxidation in which oxygen is involved is always the term of the modern definition of oxidation. However, there is another old definition of hydrogen that can be found in organic chemistry texts. This is the opposite of the definition of oxygen, so it can be confusing. It is still good to be aware. According to this definition, oxidation is the loss of hydrogen, while reduction is the gain of hydrogen.

