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Review

Metal compounds and small molecules activation – case studies

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Contents

Abbreviations: Φ_Δ, quantum yield of $^1O_2$ formation; Cbl, cobalamin; C*c*O, cytochrome *c* oxidase; cyclam, 1,4,7,9-tetraazacyclotetradecane; DNICs, dinitrosyl iron complexes; DTC, dithiocarbamate; $dtpa^{5-}$, diethylenetriaminepentaacetate; $edampda^{2-}$, *N*,*N*′-bis(2-pyridylmethyl)ethylenediamine-*N*,*N*′-diacetate; EDRF, endothelial-derived relaxing factor; $edta^{4-}$, ethylenediaminetetraacetate; FTTP, tetra(*m*-trifluoromethylphenyl)porphyrin; $hedtra^{4-}$, hydroxyethylenediaminetriacetate; IFET, interfacial electron transfer; IRP, iron regulatory protein; $mida^{2-}$, methyliminodiacetate; metMb, metmyoglobin; NADH, reduced nicotinamide adenine dinucleotide; NHase, nitrile hydratase; nta^{3-}, nitrilotriacetate; OEP, octaethylporphyrin; $P450_{cam}$, cytochrome P450 from *Pseudomonas putida*; $pida^{2-}$, 2-pyridylmethyliminodiacetate; Por, porphyrin; RBS, Roussin's Black Salt; RNOS, reactive NO species; ROS, reactive oxygen species; RRS, Roussin's Red Salt; salen, *N*,*N*′-bis(salicylidene)ethyelenediamine dianion; SNP, sodium nitroprusside; Sol, solvent; tim, 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclodeca-1,3,8,10-tetraene; TMPS, tetra(sulfonatomesityl)porphine; TmTP, tetra-*m*-tolylporphine; tpa, tris-2-pyridylmethylamine; tpen, *N*,*N*,*N*′,*N*″-tetra-(2-pyridylmethyl)ethylenediamine; TPP, tetraphenylporphyrin; TPPS, tetra(4-sulfonato-phenyl)porphine; $ttha^{6-}$, triethylenetetraaminehexaacetate

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Abstract

The activation of small molecules has a significant impact in biology, medicine, industrial catalysis and environmental protection. Two molecules, especially, oxygen and nitric oxide have attracted considerable interest for many years. Reactive oxygen species (ROS) and reactive nitric oxide species (RNOS) may be generated thermally or photochemically in systems consisting of metal compounds. In homogeneous systems metal species serve as a coordination and/or electron (eventually energy) transfer centre. In heterogeneous systems small molecules can undergo adsorption followed by electron or energy transfer processes with semiconductor participation. This review presents recent trends in studies on the metal assisted processes in which activated forms of NO or O_2 are formed and play a key biological and medical role.

Keywords: ROS; RNOS; Photosensitiser; Semiconductor; Activation; Mechanism; Bioregulation; Phototherapy; Photodetoxification; Photocatalysis

1. Introduction

Small molecule activation (NO, O_2, CO, CO_2, N_2, etc.) has attracted scientific attention for several years. It has a significant impact in biology, medicine, industrial catalysis and environmental protection. Each activation process has its own requirements depending primarily on the desired effect such as change of the reaction pathway, selectivity, effectiveness, yields, new processes or reactions which are not allowed thermodynamically and/or kinetically from the substrate ground state, lower energy input, etc. These goals could be achieved in a thermal or photochemical manner in homogeneous or heterogeneous systems as direct or indirect processes. Metal ions and compounds play a crucial role in thermal and photochemical activation of small molecules. They not only can mediate the actual active form of the small molecule, but also control its spatial concentration dynamics.

In homogeneous system an activated molecule is usually coordinated to a metal centre while in heterogeneous systems adsorption processes play a key role. The bound molecule shows different physical and chemical properties (geometry, electron density, reactivity, etc.) as compared to those of the free one. The coordinated or adsorbed molecule also has a different mobility: the bound moiety can be transported to other places where, under certain conditions, it can be released. Finally, access to a coordinated or adsorbed molecule may be limited to a certain type of substrate due to possible steric hindrance and limited size of the cavity in which the molecule is embedded. Data on the electronic and structural character of the active form as well as on the thermodynamics and kinetics of the particular activation process is necessary not only for understanding its mechanism, but also for enabling a systematic tuning of the studied systems to achieve the best results.

Considerations in this paper are focused on two biologically important molecules: nitric oxide, NO, and dioxygen, O_2. The solubility and transport properties of NO and O_2 are similar but these two molecules in their ground states display quite different reactivity. Nitric oxide, a stable-free radical with an unpaired electron in the π^* orbital, achieves a wide variety of effects through its interaction with active centres via redox and addition chemistry and therefore can be considered as one of the 'reactive nitric oxide species' (RNOS). NO can reversibly bind to a metal ion and plays the role of an electron donor or an electron acceptor. However, it is neither a strong one-electron oxidant nor a strong one-electron reductant. The properties of O_2 molecule are different. Its ground triplet state shows much lower activity and therefore must be excluded from the 'reactive oxygen species' (ROS) family. Moreover, for NO and O_2 there are different priorities for activation modes. In the case of nitric oxide electron transfer processes are the most important source of different RNOS whereas in the case of ROS, energy transfer processes are as important as electron transfer processes. ROS in systems containing metal compounds can be achieved either through thermal or photochemical paths. As a result of photochemical activation electron or energy transfer occurs. In the case of the electron transfer, radicals are mainly generated while energy transfer is responsible rather for singlet oxygen generation. This differentiation, however, is not very strict since several consecutive thermal reactions influence the formation of various ROS. An additional advantage of the application of light is the high selectivity of supported energy which cannot be realised by thermal methods. The selection of an appropriate light energy helps to achieve the desired excited state and therefore the desired activity. For instance, oxygen activation leads to formation of one of two forms of singlet oxygen, $^1\Sigma_g$ or $^1\Delta_g$, having different energy.

Coordination compounds or solid surface participating in the activation process support an appropriate reaction site. The geometry of this site may play a key role, for instance in enzymatic reactions. The metal centre controls redox properties and therefore the nature of coordinated (or chemisorbed) small molecule. In the case of photoactivated systems the presence of metal ion assures appropriate spectroscopic properties of the sensitiser. A metal ion may influence the lifetimes of a triplet excited state of a sensitiser enhancing the efficiency of small molecule photoactivation.

The aim of this paper is not to review the state of art in NO and O_2 activation research. Several excellent reviews covering these topics appeared both for NO [1–6] and O_2 [6–12] activation. Here we want to emphasise selected aspects of metal assisted RNOS and ROS generation in very different homo- and heterogeneous systems (Fig. 1). In the case of NO we focus on exemplifying the role of biological metal centres and possible applications of exogenous metal compounds in bioregulatory functions of nitric oxide and its activation by redox or substitution reactions. On the other hand, for dioxy-