Activation of Nitric Oxide and Organonitroso Complexes (X-NO) at Low-Coordinate Co, Ni, and Cu Centers

Timothy H. Warren, Pooja Kapoor, Simona C. Puiu, Marie Melzer, Matthew S. Varonka, and Douglas E. Cordeau

Georgetown University, Department of Chemistry, Box 571227, Washington, DC 20057-1227.

In a remarkably short period of time, nitric oxide has become recognized as a key molecule in biology. In addition, the biochemistry of organic nitroso compounds (X-NO) is in many ways linked to that of nitric oxide (NO). These organic derivatives can serve either as sources of NO *in vivo* or can produce similar biological effects as NO (e.g. vasodilation). Release of NO from many organonitroso compounds, however, requires a reducing equivalent for which redox active metalloenzymes have been implicated.

Employing low-coordinate, monovalent later, first row transition metal β-diketiminates as models, we explore the bonding and reactivity of three-coordinate metal-nitrosyl complexes [NN]M(NO). Alkyl and aryl *C*-organonitroso compounds (R-NO) readily add to the Ni-NO bond to give "NONOates" [NN]Ni(κ^2-O_2N_2R). Moreover, photoexcitaton of [NN]Ni(NO) with visible light allows access to η^2-NO "side-on" states with lowered ν(NO) stretching frequencies.

We also explore the reaction chemistry of these ß-diketiminato templates with C-, N-, O-, and S-organonitroso compounds X-N=O connected to the biological reactivity and availability of NO. These organonitroso derivatives exhibit diverse bonding modes and reactivity patterns with the [NN]M fragments ranging from release of NO to complete cleavage of the N=O bond. Factors that lead to *X-N*O vs. X-*N=O* bond activation will be outlined, and considered in context of the metabolism and formation of these NO-containing substances by non-heme centers.