Reactions of Cobalt Porphyrin Nitrite with Oxophilic Substrates. Formation of Sulfenic Acid by Oxygen Atom Transfer from Nitrite to Thiol.

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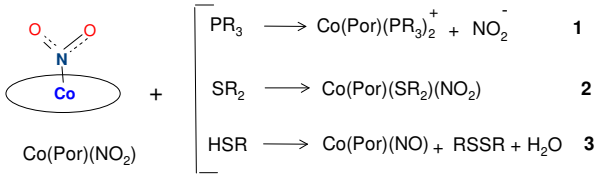
The endogenous reduction of nitrite (NO_2^-) to nitric oxide (NO) is drawing increasing attention as a protective mechanism against hypoxic injury in mammalian physiology and as an alternative source of NO, which is involved in in physiological regulation of blood flow, cell signalling and vasodilation [1]. The chemical mechanisms for this transformation, which are mediated by metallo proteins and model compounds are of considerable interest. While thiol mediated reduction of nitrite at heme-model iron porphyrins has received significant attention [2], comparatively little is known about analogous reactions at other biologically relevant metal centers. Recently we have reported that reaction of Co(TTP)(NO_2) with H_2S/ethanethiol results in formation of cobalt nitrosyl - Co(TTP)(NO) along with the formation of disulfide and H_2O via proposed proton-assisted O-atom transfer mechanism (OAT) [3]. As an intermediate formation of sulfenic acid EtS(=O)H was proposed.

Here we present the reactions of the model porphyrin nitrite Co(TTP)(NO_2) (TTP = meso-tetratolylporphyrinato dianion) in sublimated solid films with oxophilic substrates such as phosphine, sulfide and different thiols at various temperatures from 77 K to room temperature using in situ IR spectroscopy with the use ^{15}N and ^{18}O labelled and natural abundance NO_2. Reactions of nitro cobalt porphyrins with phosphine and sulfide does not show oxidation of substrate. Mass spectrometric analysis Co(TTP)($N^{18}O_2$) reactions products with thiols revealed respective disulfides and $H_2{}^{18}O$, suggesting that ^{18}O originated from coordinated nitrite. Similar experiments conducted in solution, in presence of sulfenic acid trap- dimedone and monitored by UV-Vis supports reduction Co(TTP)(NO_2) to Co(TTP)(NO). Analysis of reaction products by ESI-QTOF mass spectrometry clearly show formation of dimedone thioethers, confirming earlier suggested O-atom transfer mechanism via formation of sulfenic acid intermediate. DFT calculations of reaction coordinate diagram of OAT from Co(TTP)(NO_2) to EtSH were also performed. A scan of the approach of the thiol to the O atom with greater electronic density led to the optimization of a transition state.



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References.

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