REDUCTION OF NITRITE BY MANGANESE AND COBALT PORPHYRINS: GENERATION OF NITROSYL BY H_2S/THIOL

Garik Martirosyan [a], Astghik Hovhannisyan [a], Ashkharuhi Aleksanyan [a], Alexei Iretskii [b] and Peter C. Ford [c]

[a] Scientific and Technological Centre of Organic and Pharmaceutical Chemistry NAS, 0014, Yerevan, Armenia
[b] Department of Chemistry, Lake Superior State University, Sault Sainte Marie, MI 49783, USA
[c] Department of Chemistry and Biochemistry, University of California, Santa Barbara, Santa Barbara, CA 93106-9510, USA

Inorganic nitrite (NO_2^-) is important species in mammalian physiology with a diverse and interconnected chemical biology. Nitrite is known as a significant source of nitric oxide that acts as a vasodilator and intrinsic signaling molecule [1]. It has been shown that biological thiols (cysteine and gluthathione) reduce the water-soluble iron porphyrin nitrite through an oxygen atom transfer mechanism that leads to the formation of iron porphyrin nitrosyl and the corresponding sulfenic acid [2]. Other detailed studies demonstrated that the reaction of a similar porphyrin nitrite with hydrogen sulfide (H_2S, which is now accepted as a third signaling molecule along with CO and NO), also leads to the formation of porphyrin nitrosyl and generation of HNO and HSNO [3]. While thiol/H_2S mediated reduction of nitrite at iron porphyrins has received significant attention, comparatively little is known about analogous reactions at other biologically relevant metal centers.

Here we present the low-temperature FT-IR and Uv-Vis spectroscopic results of the reaction H_2S and EtSH with sublimed layers containing the CoTTP(NO_2) nitro and MnTTP(ONO) nitrito porphyrin complexes (TTP - meso-tetra-p-tolylporphyrin $^{2-}$). The eventual products of this reaction in both cases are the respective nitrosyl complex CoTTP(NO) and Mn(TTP)(NO) and disulfides. The mechanism of the reactions that accounts for all spectroscopic observations with the use ^{15}N and ^{18}O labeled and natural abundance NO_2 is proposed to proceed through the O-atom transfer reaction from coordinated NO_2^- to H_2S and EtSH. The transient intermediates detected upon monitoring the reaction from 77K to room temperature and final products, analyzed by mass spectrometry are discussed.

Acknowledgements: The financial support from SCS of the Republic of Armenia (Project 21AG-1D040) is gratefully acknowledged.

[1] Bueno M., Wang J., Mora A., Gladwin M. T., Antioxid. Redox Signaling 2013, 18, 1797

[2] Heinecke, J.; Ford, P. C. J. Am. Chem. Soc., 2010, 132, 9240.

[3] Miljkovic, J.; Kenkel, I.; Ivanovic´-Burmazovic, I.; Filipovic, M. Angew. Chem. Int. Ed., 2013, 52, 12061.