Abstract

Mechanistic Investigation of Sulfur Dioxide reduction using second sphere modified porphyrins

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In this work, reduction of Sulfur Dioxide (SO_2) by Iron (II) tetraphenylporphyrin ($Fe^{II}TPP$) and second sphere modified, Fe^{II} Pyridine is demonstrated. A solution of $Fe^{II}TPP$ and Fe^{II} Pydn in THF is impregnated with a saturated solution of SO_2 in THF and the resulting reaction is allowed to proceed for different time scale under different temperatures. The reaction mixture is then subjected to different spectroscopic techniques in order to elucidate the mechanism of the SO_2 reduction by $Fe^{II}TPP$. The detailed study reveals that SO_2 is reduced by $Fe^{II}TPP$ via a $2e^-/2H^+$ process, passing through a Low Spin hexacoordinated MeOH-$Fe^{III}TPP$-SO_2^- intermediate, which via a proton dependant pathway gets dehydrated and forms another Low Spin hexacoordinated MeOH-$Fe^{III}TPP$-SO intermediate. The intermediate eventually releases SO, which has been trapped as a cheletropic sulfoxide adduct of 2,3-dimethylbutadiene. This is the first report of SO_2 reduction outside protein matrix and also the first observation of two unique intermediates. All of these intermediates have been characterized spectroscopically and backed up by $^{34}S/^{32}S$ isotope dependant unique vibrational bands of the Fe-S and S-O bonds, giving veracity to our claims. These two intermediates shed light on the mechanism of the $2e^-/2H^+$ reduction of SO_2 by $Fe^{II}TPP$. Using second sphere modified Fe porphyrin with pendant Pyridine ligand to mimic the SiR distal environment, SO_2 reduction reaction mechanisms have also been investigated. In comparison to $Fe^{II}TPP$, the second sphere modified porphyrin shows markedly different rates of SO_2 reduction and also generates intermediate signals which bear similarity to the SO_2 reduction using $Fe^{II}TPP$. This strongly suggests about a second sphere interference in SO_2 reduction.

Thus, this work sheds light on the SO_2 reduction reaction mechanism using Fe porphyrins, with and without second sphere modifications and also indicates the presence of some novel intermediates, which have never been realized outside the protein matrix.

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