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By

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Interactions of hydrogen sulfide with lactoperoxidase

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Hydrogen sulfide (H_2S) has gained attention since it is implied in human physiological functions. Furthermore, H_2S interacts with physiologically important hemeperoxidases as lactoperoxidase (LPO), a relevant enzyme for the immune defense system and airway inflammation. LPO in the presence of hydrogen peroxide (H_2O_2) and H_2S forms a derivative called sulflactoperoxidase (sulfLPO). Despite all the efforts, there still a need to further comprehend the species involved in the reaction of LPO with molecular oxygen or H_2O_2in the presence of H_2S. It has been found that histidine (His) is involved in the sulfheme formation. To verify if His in other positions, or arginine that is present in the active site of LPO, forms the sulfheme derivative, mutants were performed by site directed-mutagenesis. The interactions between H_2S and the native ferric LPO as well as ferrous LPO and the oxo-ferryl intermediaries were investigated using UV-Vis spectroscopy, stopped-flow and electron paramagnetic resonance (EPR). None of the mutants form the sulfheme derivative confirming that His with the adequate orientation plays an important role in the sulfheme formation. The results presented here show that under strict anaerobic conditions the addition of H_2S to native LPO does not generate the formation of the dominant 638 nm species, indicating the need of molecular oxygen to produce this LPO derivative associated to the formation of sulfLPO. In the LPO reaction with $H_2O_2$and H_2S there is a continuous turnover in the formation of the 638 nm transition. EPR experiments indicate that sulfheme formation prevents the generation of carbon center radicals in the heme group. These results suggest that H_2S is a non-classical LPO peroxidative substrate since it modifies the heme group in a continuous turnover and that sulfheme is a reversible process, which apparently does not generate additional H_2S upon the enzymes' throughput. The implication suggests that the 638 nm species or sulfheme may not lead to a direct H_2S transport mechanism rather, H_2S in LPO acts as an unusual substrate to scavenge H_2O_2.