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Unspecific Peroxygenase can be Tuned for Oxygenase or Halogenase Activity by Controlling the Reaction pH

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PURPOSE OF THE ABSTRACT

Unspecific peroxygenases (UPOs) have gained significant interest due to their ability to catalyse the selective oxygenation of a large range of organic substrates at the expense of only hydrogen peroxide.[1]
UPOs are phylogenetically related to the heme-containing enzyme, chloroperoxidase (CPO).[2] CPO catalyses the oxidation of chloride and bromide to the corresponding hypohalous acids that can effect the halogenation of a number of organic substrates.[3,4] The structural similarity of UPOs to chloroperoxidase (CPO) means that UPOs can also catalyze halogenation reactions based upon the generation of hypohalous acids from halide and peroxide. Ullrich and Hofrichter demonstrated the halogenating capability of the UPO from Agrocybe aegerita (AaeUPO) with the bromination of phenol to from 2- and 4-bromophenol although the phenomenon was not extensively explored.[5]

Whilst investigating the halogenating activity of AaeUPO we discovered that this enzyme can be tuned for oxygenase or halogenase activity by simply controlling the pH. Here we show that using simple aromatic compounds such as thymol at pHs of 3.0 and 6.0, either brominated or oxygenated products are evolved.

In addition, we have developed a one-pot oxygenation-bromination cascade reaction using 4-ethylanisole, in which the pH is adjusted at the halfway stage, yielding the selectively brominated and oxygenated product 3'-bromo-4'-methoxyacetophenone. These results identify UPOs as an unusual example of a biocatalyst that is tunable for entirely different chemical reactions, dependent upon the reaction conditions.

FIGURES

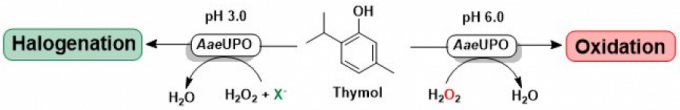

FIGURE 1

Scheme 1.

By controlling the pH of the solution, the unspecific peroxygenase from Agrocybe aegerita can be tuned for either oxygenase or halogenase activity.

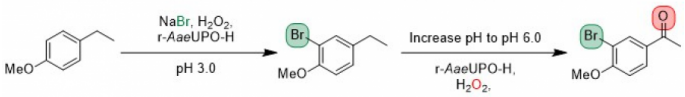

FIGURE 2

Scheme 2.

Halogenation and oxygenation cascade catalysed by rAaeUPO-PaDa-I-H.

KEYWORDS

Unspecific Peroxygenase | Halogenation | Oxygenation | Cascade

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