AMPHIPHILE-STABILIZED EMULSIONS AND IONIC LIQUIDS AS MEDIA IN HALOPEROXIDASE BIOCATALYSIS

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Chloroperoxidase from *Caldariomyces fumago* represents an exquisite biocatalyst with a broad range of applications and reactivity modes. In addition to the native halogenation properties,[1] *Cf*CPO also exhibits peroxygenase activity and thus can serve as oxygenating catalyst in a number of synthetic transformations.[2]

As part of our ongoing campaign to identify biological mediators with abilities to address synthetically important reactions beyond the biosynthetic repertoire,[3] an enzymatic halocyclization was developed that allows for the conversion of allenic alcohols and carboxylates to brominated O-heterocycles. Interestingly, the use of micellar reaction media, either stabilized by short non-ionic PEG amphiphiles or by cetyl trimethylammonium bromide proved to be of critical importance to achieve high yields in the enzymatic halogenations.[4] The multiphasic reaction media furthermore enabled direct catalytic cascades where the enzymatically generated vinyl bromides can be cross-coupled by means of palladium catalysts in Suzuki- and Sonogashira-type C-C bond-forming reactions.[5] Beyond its synthetic potential, *Cf*CPO was also investigated as biocatalyst for the decontamination of chemical warfare agents. Here, sulfur mustard-type β-chlorosulfides are readily absorbed by choline acetate that effectively trap the volatile toxins in the non-volatile ionic liquid, where *Cf*CPO (and other biocatalysts) rapidy convert the mustard simulants to less hazardous metabolites.

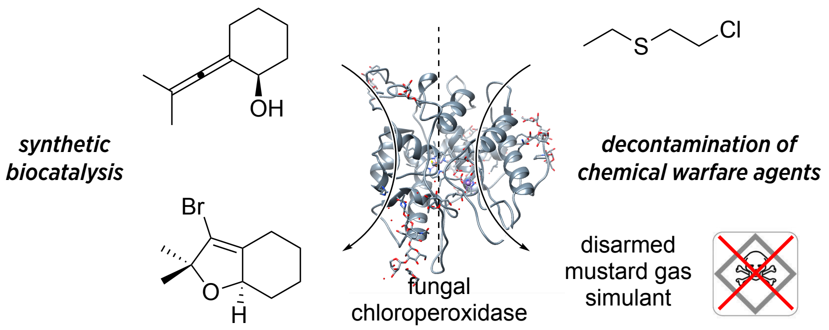

Figure 1: Fungal chloroperoxidase catalyzes bromocyclizations in micellar reaction systems (left) as well as oxidative degradation of chemical warfare agents in choline acetate.

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