BIOCATALYSIS

Enzymatic H_2O_2 for biocatalysis

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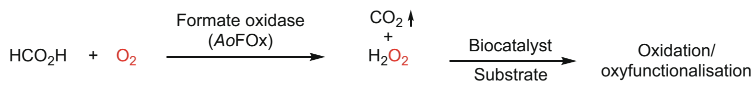

Several biocatalytic oxidation and oxyfunctionalization reactions rely on H_2O_2 — a clean oxidant — which causes inactivation of the enzymes over time. A strategy to overcome this incompatibility is to produce H_2O_2 in situ for its use in biocatalysis.

The commonly used biocatalytic H_2O_2 generation system is based on glucose oxidase, but its practicality is limited due to the high amount of produced waste (196 g of gluconate waste per mol H_2O_2 generated) and a high viscosity of the reaction medium at large scales.

Now, Frank Hollmann and colleagues tested a recently reported formic acid oxidase from *Aspergillus oryzae* (*Ao*FOx) as an alternative enzyme for in situ generation of H_2O_2 using formate as reductant. Hereby, during the reductive activation of O_2 only 44 g of volatile CO_2 waste — which does not accumulate in the reaction medium — are produced per mol H_2O_2.

First, the authors tested *Ao*FOx in a model oxyfunctionalization reaction — the selective hydroxylation of ethyl benzene into (*R*)-1-phenylethanol — catalysed by a peroxygenase from *Agrocybe aegerita* (*Aae*UPO). The authors showed that this enzymatic cascade operates optimally at pH 6 and 25 °C. A relative ratio of H_2O_2-generating and H_2O_2-consuming enzymes of 1:5 resulted in good productivities and stable product formation for at least 24 hours. Increasing the availability of O_2 was a critical factor in enabling a ten-fold increased productivity at higher O_2 pressures compared to the reaction under ambient atmosphere and without stirring.

Finally, the authors demonstrated the compatibility of the presented H_2O_2 generation system with different enzymes (cytochrome *c*, lipase B, chloroperoxidase) in biocatalytic oxidation reactions such as epoxidation, sulfoxidation and hydroxyhalogenation. Remarkably, the turnover numbers achieved with the *Ao*FOx system in these H_2O_2-dependent reactions proved to be orders of magnitude higher compared to the utilization of established H_2O_2 generation systems.

Overall, the *Ao*FOx H_2O_2 generation system is simple, practical and shows excellent performance and good compatibility in coupled H_2O_2-dependent reactions. This system can be further engineered towards a lower K_m value towards formate or a broader optimal temperature range.

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