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Enantioselective Photobiocatalytic Hydroxylation of Ethylbenzene.

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Motivation

- Enzymes are highly selective & efficient
- Especially Peroxidases & Peroxygenases:
  - Catalyze interesting oxyfunctionalizations
  - Use economically prized H_2O_2 as co substrate

but:

- Have a poor stability against H_2O_2[1]

→ *In situ* H_2O_2 generation is essential

→ Combination with photocatalysis offers concentration control & homogeneous allocation of H_2O_2 under mild conditions[2]

Fig. 1 Schematic representation of the photobiocatalytic model reaction.

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Set-up

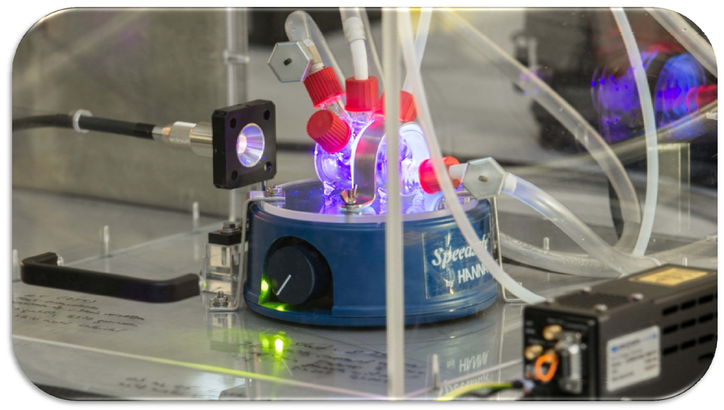

Fig. 2: Reaction set-up: 365 nm adjustable & collimated LED, up to 145 mW cm^{-2} / 5.8 mE L^{-1} min^{-1}, 0_2-saturated, 14 ml glass reactor with a 3.14 cm^2 illumination window.

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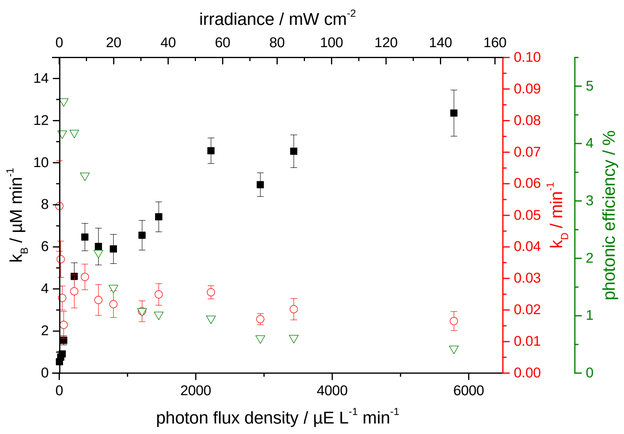
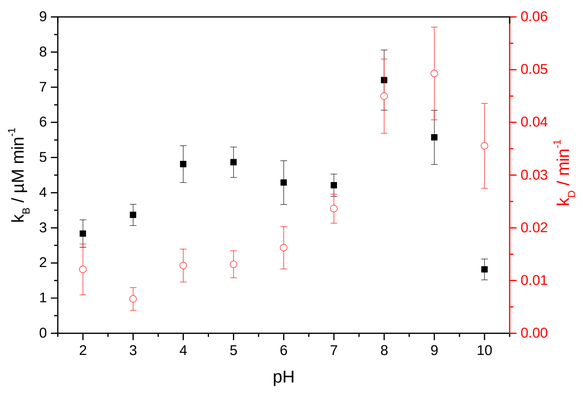
Photocatalytic H_2O_2 generation

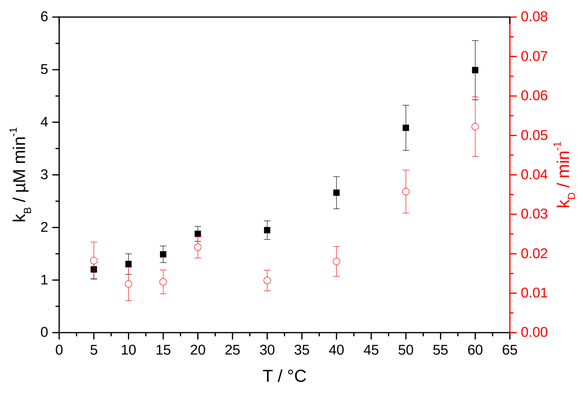
Light Intensity



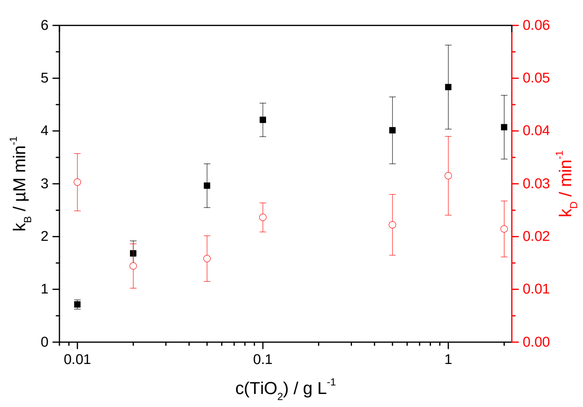
pH



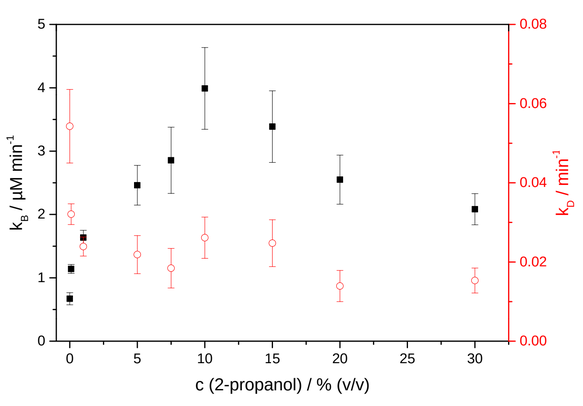
Temperature



Catalyst quantity



2-Propanol amount



Oxygen content

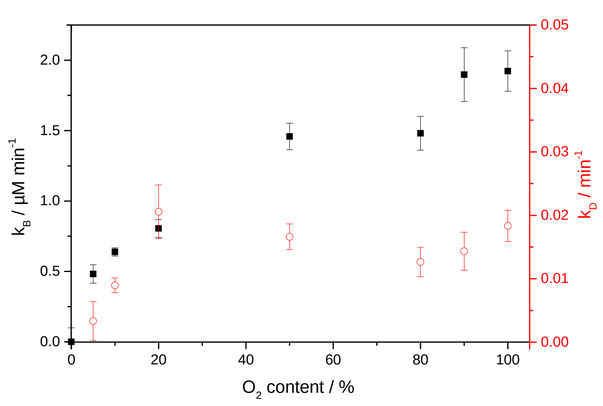


Fig. 3: Estimated generation (▪) and degradation (◦) rates of photocatalytic H_2O_2 formation in dependence of pH, temperature, catalyst quantity, amount of 2-propanol, oxygen content and light intensity as well as photonic efficiency (▽). Parameters unless varied: λ=365 nm, 5.5 mW cm^{-2}, O_2-bubbled, 0.1 g l^{-1} TiO_2 (Evonik P25) 0.1 M phosphate, 25°C pH = 7.0, 10% (v/v) 2-propanol. The photon flux was determined via ferrioxalate actinometry.[3] H_2O_2 concentrations were measured using an adapted fluorometric enzyme assay.[4]

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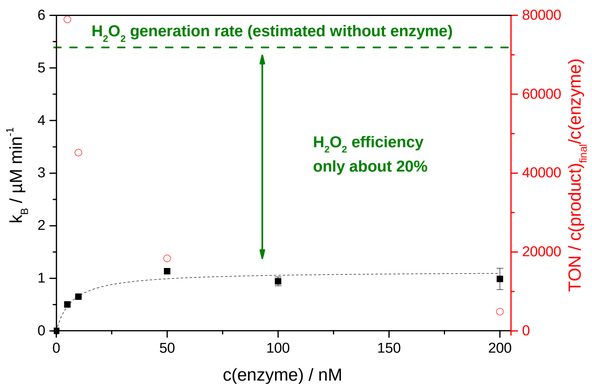
Photobiocatalysis

Enzyme amount



Enzyme stability

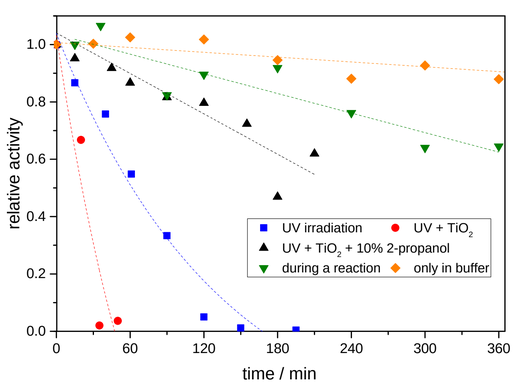


Fig. 4: Generation rate (k_B, ▪) and turnover number (TON, ◦) of the photobiocatalytic (R)-1-phenylethanol formation in comparison with the H_2O_2 generation rate (left) and enzyme stability testing under various conditions (right). Reaction parameters unless varied: λ=365 nm, 16.4 mW cm^{-2}, 0.1 g l^{-1} TiO_2 (Evonik P25) 0.1 M phosphate, 25°C pH = 7.0, 10% (v/v) 2-propanol, 10 mM ethyl benzene, 100 nM *Aae*UPO.

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Conclusion

- H_2O_2 generation rates can be increased by raising the light intensity, but photonic efficiency drops exponentially
- The process parameters: pH, temperature, c(TiO_2), c(2-propanol) and c(O_2) have a big impact on the H_2O_2 generation and degradation rates
- Photobiocatalytic (R)-1-phenyl ethanol generation is possible

→ Further optimization of photo- & biocatalytic interactions

→ Understanding of the enzyme inactivation parameters

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References

[1] Bormann *et al.*, Catal. Sci. Technol., 2015, 5, 2038-2052.
[2] W. Zhang, B. O. Burek *et al.,* Angew. Chem. Int. Ed., 2017, doi: 10.1002/anie.201708668.
[3] C. G. Hatchard, C. A. Parker, Proc. R. Soc. A Math. Phys. Eng. Sci., 1956, 235, 518–536.
[4] G. G. Guilbault *et. al.*, Anal. Chem., 1968, 40, 1256–1263.