

## Einladung zu einem Kolloquium

### Hörsaal HCI J3

### ETH Zürich, Hönggerberg

Datum/Zeit: **Dienstag, 14. Mai 2024, 16.45 Uhr**

Referent: **Prof. Peter R. Schreiner**  
Justus-Liebig-Universität Giessen, Giessen, Deutschland

Titel: **Rethinking Chemistry: The Role of Quantum Mechanical Tunneling<sup>[1]</sup>**

Quantum mechanical tunneling (QMT) is a result of the wave nature of particles that implies that a particle penetrates a potential energy barrier even though there is insufficient energy. This has serious consequences for chemical reactions, which has, not been appreciated much. In the last years has it become clear just how important QMT is for understanding chemical reactions. Here we emphasize the role that QMT plays in reactions of exemplary molecules. Once fully understood, the control<sup>[2]</sup> and application of tunneling in chemical synthesis, possibly stimulated through catalysts<sup>[3]</sup> or energy transfer, will open fascinating new ways of conducting chemical reactions.

We also expose QMT as the third reaction paradigm that can overwrite traditional kinetic control and govern reactivity, which we term *tunneling control*.<sup>[4]</sup> These findings are exemplified with the first experimental isolation and full spectroscopic and theoretical characterization of the elusive hydroxycarbenes (R-C-OH)<sup>[5]</sup> that undergo facile [1,2] hydrogen QMT to the corresponding aldehydes under high barriers. We will demonstrate that this is a general phenomenon,<sup>[4b,6]</sup> as exemplified by other OH-tunneling examples such as the rotational isomerization of a variety of carbocyclic acids.<sup>[7]</sup> Such tunneling processes do not merely represent corrections to the reaction rate, they *are* the reaction rate, i.e., the completely *control* the reaction outcome.<sup>[8]</sup> They can also override common notions such as the often-invoked Curtin-Hammett principle.<sup>[9]</sup>

We also demonstrate that *competitive carbon vs. nitrogen QMT* completely determines the outcome of some selected organic chemical reactions.<sup>[10]</sup> Additionally, we show that even CO<sub>2</sub> activation can occur through a tunneling process of the entire CO<sub>2</sub> molecule.<sup>[11]</sup>

Finally, we will suggest that we need a fresh look at the role of the barrier width in chemical reactions by introducing the notion of "*intrinsic barrier width*" that has not been defined before.<sup>[12]</sup>

[1] P. R. Schreiner, *Trends Chem.* **2020**, *2*, 980. (prs@uni-giessen.de)

[2] J. P. L. Roque, C. M. Nunes, L. P. Viegas, N. A. M. Pereira, T. M. V. D. Pinho e Melo, P. R. Schreiner, R. Fausto, *J. Am. Chem. Soc.* **2021**, *143*, 8266.

[3] S. Henkel, M. Prado Merini, E. Mendez-Vega, W. Sander, *Chem. Sci.* **2021**, *12*, 11013.

[4] a) P. R. Schreiner, *J. Am. Chem. Soc.* **2017**, *139*, 15276; b) D. Ley, D. Gerbig, P. R. Schreiner, *Chem. Sci.* **2013**, *4*, 677; c) D. Ley, D. Gerbig, P. R. Schreiner, *Org. Biomol. Chem.* **2012**, *19*, 3769; d) P. R. Schreiner, H. P. Reisenauer, D. Ley, D. Gerbig, C.-H. Wu, W. D. Allen, *Science* **2011**, *332*, 1300.

[5] a) D. Gerbig, H. P. Reisenauer, C.-H. Wu, D. Ley, W. D. Allen, P. R. Schreiner, *J. Am. Chem. Soc.* **2010**, *132*, 7273; b) D. Gerbig, D. Ley, H. P. Reisenauer, P. R. Schreiner, *Beilstein J. Org. Chem.* **2010**, *6*, 1061;

c) P. R. Schreiner, H. P. Reisenauer, F. C. Pickard IV, A. C. Simmonett, W. D. Allen, E. Mátyus, A. G. Császár, *Nature* **2008**, *453*, 906; d) P. R. Schreiner, H. P. Reisenauer, *Angew. Chem. Int. Ed.* **2008**, *47*, 7071; e) B. Bernhardt, M. Ruth, A. K. Eckhardt, P. R. Schreiner, *J. Am. Chem. Soc.* **2021**, *143*, 3741.

[6] a) D. Ley, D. Gerbig, J. P. Wagner, H. P. Reisenauer, P. R. Schreiner, *J. Am. Chem. Soc.* **2011**, *133*, 13614; b) D. Gerbig, D. Ley, P. R. Schreiner, *Org. Lett.* **2011**, *13*, 3526.

[7] a) S. Amiri, H. P. Reisenauer, P. R. Schreiner, *J. Am. Chem. Soc.* **2010**, *132*, 15902; b) D. Gerbig, P. R. Schreiner, *J. Phys. Chem. B* **2014**, *119*, 693; c) M. M. Linden, J. P. Wagner, B. Bernhardt, M. A. Bartlett, W. D. Allen, P. R. Schreiner, *J. Phys. Chem. Lett.* **2018**, *9*, 1663; d) J. P. Wagner, H. P. Reisenauer, V. Hirvonen, C.-H. Wu, J. L. Tyberg, W. D. Allen, P. R. Schreiner, *Chem. Commun.* **2016**, *52*, 7858; e) H. P. Reisenauer, J. P. Wagner, P. R. Schreiner, *Angew. Chem. Int. Ed.* **2014**, *53*, 11766.

[8] P. R. Schreiner, H. P. Reisenauer, D. Ley, D. Gerbig, C.-H. Wu, W. D. Allen, *Science* **2011**, *332*, 1300.

[9] A. Mardyukov, H. Quanz, P. R. Schreiner, *Nat. Chem.* **2017**, *9*, 71.

[10] C. M. Nunes, A. K. Eckhardt, I. Reva, R. Fausto, P. R. Schreiner, *J. Am. Chem. Soc.* **2019**, *141*, 14340.

[11] B. Bernhardt, M. Schauerhann, E. Solel, A. K. Eckhardt, P. R. Schreiner, *Chem. Sci.* **2022**, *14*, 130.

[12] G. Qiu, P. R. Schreiner, *ACS Cent. Sci.* **2023**, in press. DOI: 10.1021/acscentsci.3c00926.

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**Gäste sind willkommen**