Ben-Gurion University of the Negev

אוניברסיטת בן גוריון בנגב

Special Seminar

Department of Chemistry

Tuesday, May 16, 2023

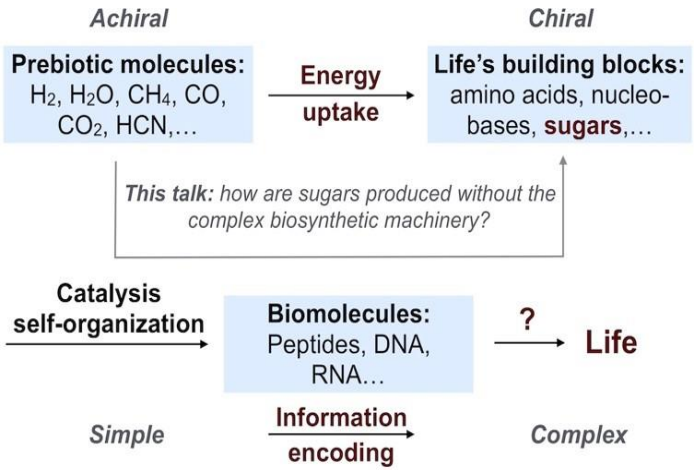
Time: 13:00

Bldg. 43 Room 015

Prof. Peter R. Schreiner

Institute of Organic Chemistry, Justus Liebig University, Heinrich-Buff-Ring 17, 35392 Giessen, Germany, prs@uni-giessen.de, ORCID: 0000-0002-3608-5515

Cool Organic Chemistry: Toward C, H, O Systems Chemistry



Although the simplest sugar, glycolal- dehyde ($HOCH_2CHO$), has been generated in the lab from its constituents[1] but also has been found on comet 67P (as evident from the *Rosetta* mission and the *Philae* lander)[2] and is suggested to occur in the *formose*[3] (Butlerow[4]) reaction, themechanism for the dimerization of two H_2CO molecules to glycolaldehyde and on to higher sugars is a riddle *to date*; thefinding of "glycolaldehyde autocatalysis" does not explain the fundamentalchemistry, requires the presence of liquid water, a strong base, high reactant concentrations, and ambient temperatures – all conditions unlikely to be present on early Earth or in extraterrestrial environments.[5]

We focus on non-aqueous reactions, ideally starting directly from the photoreaction of CO and H_2 to give hydroxymethylene ($HCOH$[6]): Under appropriate conditions H_2CO and HCOH react to glycolaldehyde and glyceraldehyde.[7] Similarly, we demonstrate that glycolaldehyde and H_2CO form a new 1,3-dioxolane that may well be the photostable storage form of these two key molecules.[8] Finally, with "*time- compression experiments*" we demonstrate the formation of glyoxylic[9] and piruvic acid[10] under conditions mimicking those of interstellar water ices doped with CO or CO_2.

In the process of uncovering these reactions, we also discovered and conceptualized the third reactivity paradigm (next to thermodynamic and kinetic control), namely *tunneling control*[6b, 11] of chemical reactions, which affects how reactions occur in extraterrestrial environments but are also relevant to

synthetic reaction planning. “

Overall, “cool organic chemistry” (chemistry at very low temperatures) enables the preparation of some very fundamental molecules relevant to the origin of life.[12]

References:

[1] D. T. Halfen, A. J. Apponi, N. Woolf, R. Polt, L. M. Ziurys, *Astrophys. J.* **2006**, *639*, 237.

[2] a) F. Goesmann, H. Rosenbauer, J. H. Bredehoft, M. Cabane, P. Ehrenfreund, T. Gautier, C. Giri, H. Kruger, L. Le Roy, A. J. MacDermott, S. McKenna-Lawlor, U. J. Meierhenrich, G. M. M. Caro, F. Raulin, R. Roll, A. Steele, H. Steininger, R. Sternberg, C. Szopa, W. Thiemann, S. Ulamec, *Science* **2015**, *349*, aab0689; b) J.-P. Bibring, M. G. G. T. Taylor, C. Alexander, U. Auster, J. Biele, A. E. Finzi, F. Goesmann, G. Klingelhoefer, W. Kofman, S. Mottola, K. J. Seidensticker, T. Spohn, I. Wright, *Science* **2015**, *349*, 493-493.

[3] R. Breslow, *Tetrahedron Lett.* **1959**, 22-26.

[4] A. Butlerow, *Liebigs Ann. Chem.* **1861**, *120*, 295-298.

[5] R. Shapiro, *Origins of life and evolution of the biosphere* **1988**, *18*, 71-85.

[6] a) 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- 909; b) P. R. Schreiner, H. P. Reisenauer, D. Ley, D. Gerbig, C.-H. Wu, W. D. Allen, *Science* **2011**, *332*, 1300–1303.

[7] A. K. Eckhardt, M. M. Linden, R. C. Wende, B. Bernhardt, P. R. Schreiner, *Nat. Chem.* **2018**, *10*, 1141-1147.

[8] A. K. Eckhardt, R. C. Wende, P. R. Schreiner, *J. Am. Chem. Soc.* **2018**, *140*, 12333-12336.

[9] A. K. Eckhardt, A. Bergantini, S. K. Singh, P. R. Schreiner, R. I. Kaiser, *Angew. Chem. Int. Ed.* **2019**, *58*, 5663-5667.

[10] N. F. Kleimeier, A. K. Eckhardt, P. R. Schreiner, R. I. Kaiser, *Chem* **2020**, *6*, 3385-3395.

[11] a) P. R. Schreiner, *Trends Chem.* **2020**, *2*, 980-989; b) P. R. Schreiner, *J. Am. Chem. Soc.* **2017**, *139*, 15276-15283.

[12] a) V. Paczelt, R. C. Wende, P. R. Schreiner, A. K. Eckhardt, *Angew. Chem. Int. Ed.* **2023**, *62*, e202218548; b) A. Mardyukov, R. C. Wende, P. R. Schreiner, *Chem. Commun.* **2023**, *59*, 2596-2599; c) B. Bernhardt, M. Schauermann, E. Solel, A. K. Eckhardt, P. R. Schreiner, *Chem. Sci.* **2022**, *14*, 130-135; d) A. Mardyukov, F. Keul, P. R. Schreiner, *Angew. Chem. Int. Ed.* **2021**, *60*, 15313-15316.