Hessisches Kompetenzzentrum
für Hochleistungsrechnen

Gas-Phase Sugar Formation Using Hydroxymethylene as the Reactive Formaldehyde Isomer

Introduction

Carbohydrates "$(CH_2O)_n$" or sugars are the formal adducts of carbon (atoms) to water with a repeating unit that structurally resembles "H–C–OH" (hydroxymethylene, **3a**). Although hydroxymethylene has been suggested as a viable building block for sugar formation, it is a reactive species that had escaped its detection until recently.[1]

Results

Here we demonstrate that formaldehyde (**2a**) reacts with its constitutional isomer hydroxymethylene to give glycolaldehyde (**1a**) in a nearly barrierless reaction.[2] This carbonyl-ene-type transformation operates in the absence of base and solvent at cryogenic temperatures similar to those found in extraterrestrial environments or interstellar molecular clouds. Hydroxymethylene acts as a building block for an iterative sugar synthesis as we demonstrate through the formation of the triose glyceraldehyde (**5a**). The results, therefore, provide a link between the well-known formose (Butlerow) reaction and sugar formation under non-aqueous conditions.[3-4] High-level *ab initio* coupled cluster computations confirm our proposed nearly barrierless carbonyl-ene-type reaction.

Project Manager
Prof. Dr. Peter R. Schreiner

Researchers
André K. Eckhardt, Michael Linden, Raffael C. Wende, Bastian Bernhardt and Prof. Dr. Peter R. Schreiner

Principal Investigator
Prof. Dr. Peter R. Schreiner

Project Term
2016 - 2019

Project Areas
Molecular Chemistry

Clusters
Skylla Cluster Gießen, Goethe-HLR Frankfurt, FUCHS-CSC Frankfurt

Software
GAUSSIAN

Additional Software
cfour

Institute
Institute of Organic Chemistry

University
Justus Liebig University Giessen

Funded by

Fonds der Chemischen Industrie

Volkswagenstiftung

Reference

[1] Schreiner, P. R., Reisenauer, H. P., Pickard Iv, F. C., Simmonett, A. C., Allen, W. D., Mátyus, E., & Császár, A. G. (2008): Capture of hydroxymethylene and its fast disappearance through tunnelling. Nature, 453(7197), 906. https://doi.org/10.1038/nature07010

[2] Eckhardt, A. K., Linden, M. M., Wende, R. C., Bernhardt, B., & Schreiner, P. R. (2018): Gas-phase sugar formation using hydroxymethylene as the reactive formaldehyde isomer. Nature chemistry, 10(11), 1141. https://doi.org/10.1038/s41557-018-0128-2

[3] Butlerow, A. (1861): Bildung einer zuckerartigen Substanz durch Synthese. Justus Liebigs Annalen der Chemie, 120(3), 295-298. https://doi.org/10.1002/jlac.18611200308

[4] Breslow, R. (1959): On the mechanism of the formose reaction. Tetrahedron Letters, 1(21), 22-26. https://doi.org/10.1016/S0040-4039(01)99487-0

Last Update: 2021-07-27 19:15