Introduction & Motivation

The mechanism for the uncatalyzed dimerization of two formaldehyde (2a) molecules to glycolaldehyde (1a) and further to higher sugars is a riddle to date (Scheme 1). While 1a has been detected in interstellar media, we prepared simple sugars in iterative gas phase formose-type reactions under interstellar conditions via highly reactive hydroxymethylene as Breslow’s ‘active formaldehyde’ isomer.

Results & Discussion

We performed two types of experiments, namely quantitative flow pyrolysis (FP) combined with standard 1H and 13C NMR analysis as well as high-vacuum flash pyrolysis (HVFP) experiments coupled with matrix isolation IR spectroscopy in solid argon at cryogenic temperatures. High-level coupled cluster ab initio computations confirm our proposed nearly barrierless ‘carbonyl ene’ reaction mechanism and experimental results.

Figure 1 | Home-build flow pyrolysis (FP) apparatus (top left) and cryogenic matrix isolation apparatus (bottom right).

Figure 2 | Reaction of methylhydroxycarbene (3b), generated by high-vacuum flash pyrolysis (HVFP) of pyruvic acid (4b), with formaldehyde (2a) to hydroxycetone (1c) via a barrierless ‘carbonyl ene’ reaction at cryogenic temperatures under matrix isolation conditions in solid argon. The C–H insertion product lactaldehyde (1b) was experimically not observed.

Figure 3 | 1H NMR spectra of products resulting from the FP of glycolic acid (4a).

Figure 4 | Computed potential energy surface for the formation of glycolaldehyde via hydroxymethylene and formaldehyde. The ‘carbonyl ene’ reaction is nearly barrierless.

Conclusions & Outlook

The simplest aldoses, glycolaldehyde and glyceraldehyde, can form directly via an essentially barrierless iterative ‘carbonyl ene’ reaction of hydroxymethylene with the corresponding aldehyde. This is an alternative concept for interstellar glycolaldehyde and subsequent sugar formation.

Literature