

# Energetics and mechanisms of the unimolecular dissociation of the protonated trioses

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The most basic units of biologically important carbohydrates ( $C_m(H_2O)_n$ ) – monosaccharides – can be viewed as oligomers and polymers of formaldehyde,  $(CH_2O)_n$ . In living organisms monosaccharides acts both as energy carriers and key components of information storage molecules.

The belief that monosaccharides are built up by formaldehyde units is not a theoretical construction. Butlerov demonstrated in 1861 that formaldehyde oligomerizes into glycoaldehyde, glyceraldehyde and higher carbohydrates in basic solution, the so-called formose reaction.

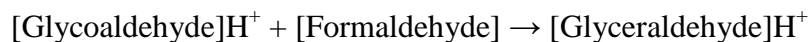
The paradigm of interstellar and prebiotic chemistry is that life evolved from small molecules that formed larger molecules. The question arises if there exist gas phase ion-molecule reactions analogous to the formose reaction, in other words if there exist interstellar pathways to sugar molecules.

We used a rewarding strategy, studied the reverse reaction – the spontaneous unimolecular dissociation of the target molecule. In this way, possible reactant molecules leading to the target may be identified, and details of the energy landscape of the reactions may be revealed.

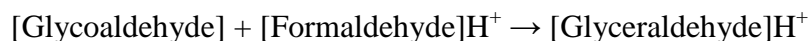
The acid catalysed formose reaction may become feasible once the other reactant has a carbon atom of opposite polarity to formaldehyde. This is possible for other aldehydes but formaldehyde, and the principle is utilized in the well known aldol reaction. In order to test out this hypothesis we have studied the fragmentation characteristics of the higher homologues, protonated glyceraldehyde and protonated dihydroxyacetone.

Our study is twofold, applying mass spectrometry to provide experimental evidence and performing a computational quantum chemical survey of the appropriate potential energy surfaces.

According to a theoretical model provided formaldehyde loss is dominating, in full agreement with experimental observation. The reverse process



is found to be obstructed by a barrier of  $20 \text{ kJmol}^{-1}$ , which will effectively block it out under interstellar conditions. On the other hand the complementary reaction



faces no such barrier.