

**UNUSUAL SYNTHESIS OF CARBOHYDRATES.** H. Barcena<sup>1,2</sup> and H. C. Connolly Jr.<sup>1,2,3,4</sup> <sup>1</sup>Dept. Physical Sci., Kingsborough Community College of CUNY, Brooklyn NY 11235; <sup>2</sup>Dept. Earth & Planet. Sci., AMNH, New York, NY 10024 USA; <sup>3</sup>Dept. of Earth and Environmental Sciences, The Graduate Center of CUNY <sup>4</sup>LPL, University of Arizona, Tucson, AZ 85721, USA. Homar.Barcena@kbcc.cuny.edu

**Introduction:** The chemistry of carbon outside our planet is subject to much conjecture as it could have implications to hypotheses on the origin of life. Specifically, the provenance of biogenic carbohydrates that have been found in meteorites and in interstellar systems is primarily questioned. We have previously examined the apparent mass-independent oxygen isotope fractionation observed in chondritic components, and propose that the non-terrestrial fractionation is due to mass-dependent fractionation resulting from a vibrational (V-V) coupling of excited carbon monoxide molecules. The resulting Boudouard disproportionation produced isotopically heavy carbon dioxide and carbon suboxide polymers, the former forming ices that serve as reservoirs for heavy isotopes of oxygen and carbon.[1,2] Subsequently, the CO<sub>2</sub> ices then react with hydrogen in a reverse water-gas shift reaction in the hot regions of the protosun to give methane and higher hydrocarbons.

Carbon chemistry is central to our model, which starts with the formation of CO<sub>2</sub> ices and higher carbon compounds from the diatomic CO. Herein, we further develop our model by showing that carbohydrate synthesis can come from CO<sub>2</sub> ices. Glycoaldehyde is a simple two-carbon carbohydrate that is the precursor to monosaccharides and more complex sugars. There have been many demonstrations of the production of higher sugars from glycoaldehyde employing different catalysts,[3] however the mechanism for its initial formation from formaldehyde is yet unknown.[4, 5]

Glycoaldehyde was detected in astronomical observations, most notably in dense molecular cores.[6] However, the origins of this molecule is still under debate and the hypotheses for its formation include gas, surface, and grain mantle chemistry, and involve UV photolysis or activation with cosmic-ray particles.[7] That this sugar precursor is found in molecular clouds hints its formation must be closely related to the earliest events in Solar System formation, and understanding these conditions could open up the diversity of organic chemistry that can occur, which we may correlate with the complex molecules that are spectroscopically detected in Sagittarius B2(N) and found in carbonaceous meteorites. We present a hypothesis on presolar carbon chemistry and show an unusual synthesis of carbohydrates herein.

**Hypothesis:** Ices of CO<sub>2</sub> have been detected in molecular clouds which we propose to have originated

from V-V coupling of CO. As these ices accumulate, they trap other molecules present in the nebula such as water, simple amines (ammonia, methylamine), nitriles (CN) low molecular weight alcohols (methanol, ethanol) formaldehyde (CH<sub>2</sub>O), acetone ((CH<sub>3</sub>)<sub>2</sub>CO) and acetic acid (CH<sub>3</sub>CO<sub>2</sub>H). Thus, CO<sub>2</sub> ice serves a two-fold purpose, first as a means to condense molecules that would be dispersed in space otherwise, and second as a medium that allows reactions to occur.

Most chemical reactions however occur in a liquid phase. The presence of fluid in the CO<sub>2</sub> ices is hypothesized to occur in two ways. First, by microwave irradiation, which excites molecules with a dipole (i.e., water and ammonia) but is not absorbed by the CO<sub>2</sub> ice, which has a zero net dipole. Water and ammonia can thus act as solvents for formaldehyde to react. As formaldehyde also has a dipole, it can absorb microwave radiation to overcome the activation energy needed for its reaction to form glycoaldehyde.

The second source of fluid in CO<sub>2</sub> ices is the liquefaction of CO<sub>2</sub> under pressure, which we speculate can occur during impact collisions or under gravitational pressure within large ice bodies (e.g. icy planetesimals or early-stage Kuiper-belt objects). Liquid CO<sub>2</sub> can act as a solvent for trapped molecules to be precursors of complex organic molecules. In the case of the reaction of formaldehyde to form glycoaldehyde, pressure can drive the entropically disfavored reaction forward, giving nonvolatile products from volatile starting materials.

**Results and Discussions:** Preliminary experiments employing frozen mixtures of water, formaldehyde, methylamine, cyanide salts, acetic acid, methanol, and other small molecules were performed under ~5 atm total pressure in liquid CO<sub>2</sub>. After the reaction, the mixture extracted with deuterated chloroform (CDCl<sub>3</sub>). The organic extract was dried with CaCl<sub>2</sub> pellets before taking the <sup>1</sup>H and <sup>13</sup>C NMR.

In the simplest experiment, commercial formaldehyde solution was used. Appearance of signals in the aliphatic region indicates the homologation of formaldehyde. The number of unique protons is not accounted by paraformaldehyde, its polymer product, which shows only a single peak in the <sup>1</sup>H NMR. Although there is a small aldehyde peak at 8.9 ppm, it is negligible in concentration. Rather, the spectra show downfield signals at 4.7-4.9 ppm. The splitting pattern is complex, however we discern that there is a coupling

constant of 2.7 Hz which could indicate  $^3J_{ae}$  in a six-membered ring for the peak at 4.9 ppm. This signal is also coupled to the 4.8 ppm ( $^2J_{HH} = 7.8$  Hz) signal, which also shows second-order coupling. Both signals integrate to one proton each, giving further evidence that they may be geminal. A third proton at 4.7 ppm also shows second-order coupling. Although no purification was performed, we believe these signals belong to one molecule because of the coupling constants, which hint to a ring structure that has axial-equatorial coupling as well as geminal coupling. More interestingly, the signals are highly deshielded, indicating the presence of electron-withdrawing groups such as alcohols. Their chemical shifts are reminiscent of sugars, however, because the geminal protons are more deshielded, we hypothesize that this is a glycoaldehyde dimer, with the anomeric proton at 4.7 ppm.[8] Full analysis requires other spectroscopic techniques, particularly since this dimer can exhibit mutarotation and have different conformations in solution.

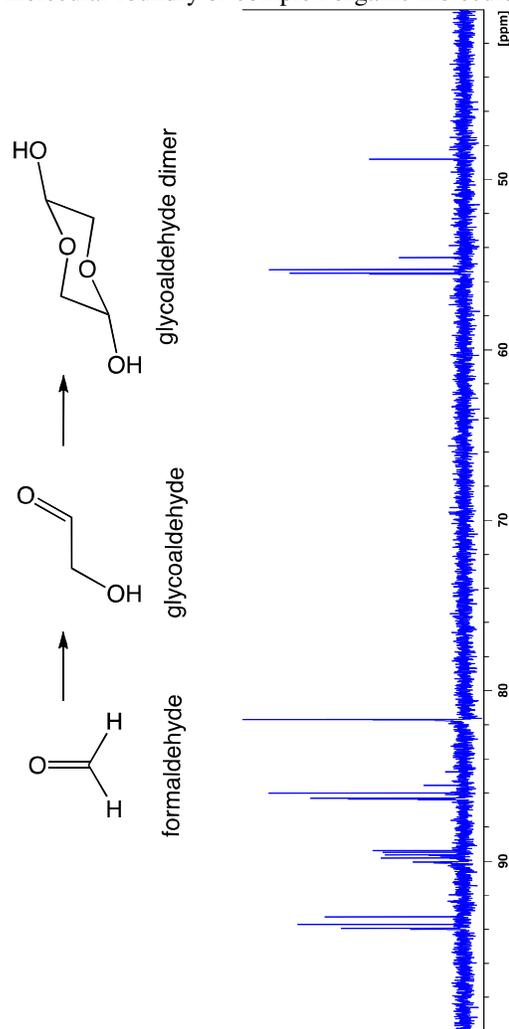
The signal at 3.3 ppm does not seem to be coupled to the signals discussed above, although they also show second-order coupling. If taken as another molecule, there are five protons, with one doublet that has a large coupling constant of 17 Hz, again indicative of geminal coupling in a ring. The more upfield shift could indicate the absence of alcohol groups that are axial or equatorial in the ring.

The  $^{13}\text{C}$  NMR in figure 1 confirms the presence of aliphatic carbons functionalized with alcohols. There are no peaks above 190 ppm that would indicate aldehydes, ketones, nor carboxylic acid derivatives. However, we assign the peaks at 90-100 ppm as indicative of hemiacetals or acetals, inasmuch as they do with common sugars.[9] The  $^{13}\text{C}$  NMR further confirms the presence of diverse chemical environments, and likely to come from more than one product.

Five- and six-membered rings in sugars result from a hemiacetal formation to give pyranose and furanose, respectively. The product tested positive for a 2,4-DNP test, confirming the presence of aldehydes or ketones, which we hypothesized to be present as a cyclic hemiacetal. Tollen's test gave a positive result as well, indicating that the products have similar reactivity to reducing sugars.

**Implications:** We have shown the feasibility of condensation reactions from pressurized cryogenic solutions. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra indicate diverse chemical environments characteristic of a mixture and in the case herein, cyclic hemiacetals. We believe that the products we obtained are carbohydrates. These carbohydrates must come from condensations of glycoaldehyde (or glycoaldehyde dimer).[5] Thus, high pressure chemistry could provide a previously unex-

plored mechanism for the formation of this primitive molecule. Although applicable to icy bodies within our Solar System, we specifically draw attention to the  $\text{CO}_2$  ices that formed before nebular collapse as a primordial molecular foundry of complex organic molecules.



**Figure 1.** Aliphatic region of the  $^{13}\text{C}$  NMR in  $\text{D}_2\text{O}$  for the product of formaldehyde solution in liquid  $\text{CO}_2$  at 5 atm. Each peak indicates a carbon in a unique chemical environment.

**References:** [1] Barcena, H. and Connolly, H.C.C. Jr. (2012) *ApJ*, 754, L32. [2] Barcena, H. and Connolly, H.C.C. Jr. (2012) *MetSoc*, Abstract #5293. [3] Iqbal, Z. and Novalin, S. (2012) *Curr. Org. Chem.*, 16, 769. [4] Breslow, R. (2011) *Tet. Lett.*, 52, 4228. [5] Breslow, R. (1959) *Tet. Lett.*, 21, 22. [6] Hollis, J. M. et. al. (2000) *ApJ* 540, L107. [7] Woods, P. M. et. al. (2012) *ApJ*, 750, 19. [8] Kobayashi, Y. and Takahashi, H. (1979) *Spectrochim. Acta*, 35A, 307. [9] Bubb, W. (2003) *Concepts Magn. Res.* 19A, 1.