

SHOCK SYNTHESIS OF ORGANICS FROM SIMPLE ICE MIXTURES? M. C. Price¹, M. J. Burchell¹, K. Miljkovic^{2,3}, A. T. Kearsley⁴ and M. J. Cole¹. ¹School of Physical Sciences, University of Kent, Canterbury, CT2 7NH, UK (mcp2@star.kent.ac.uk). ²Dept. of Earth Sciences, University College London, London, WC1E 6BT, ³PSSRI, The Open University, Milton Keynes, MK7 6AA. ⁴IARC, Department of Mineralogy, Natural History Museum, London, SW7 5BD.

Introduction: Several recent announcements of: i) the discovery of glycine on the comet 81P/Wild-2/P [1, 2]; ii) the successful shock synthesis of prebiotic compounds from liquid targets [3] and, iii) the results of molecular dynamics simulations demonstrating that amino acids could be created via shock synthesis of ices [4], have prompted a sequence of impact experiments using a light gas gun (LGG) at the Univ. of Kent [5]. The purpose of these experiments is to attempt to synthesise organic compounds from a mixture of simple ices (CO₂, NH₃ and H₂O).

NH₃ compounds, CO₂ and H₂O ices in the Saturnian system: According to observations made by Cassini's Visual and Infrared Mapping Spectrometer (VIMS) instrument, Enceladus' surface is composed mostly of nearly pure water ice except near its south pole, where there are light organics, CO₂, and amorphous and crystalline water ice. The absorptions near 3.44 and 3.53 μm could be due to short-chain organics, but other features in the spectrum are still unidentified [5]. Remote IR acquired new high-resolution spectra of Iapetus, Tethys, Enceladus and Rhea that show the absorption feature of ammonia hydrate [6]. It thus seems probable that there are conditions on the surfaces of bodies in the Saturnian system where ammonium compounds, CO₂ and water ice co-exist in a solid form. Impact of a bolide traveling with sufficiently high velocity onto such a surface, should impart enough energy to promote shock synthesis of more complex organic compounds, including amino acids, from these ices.

Laboratory experiments: Targets were prepared as follows: CO₂ ice (commercially purchased from BOC Ltd., stored in a freezer at a temperature of -130 °C) was repeatedly passed through a clean domestic ice crusher until the fragments' largest dimension was no bigger than ~3 mm. The crushed CO₂ ice was then placed in a lidded (135 mm x 95 mm x 110 mm) polystyrene box. 150 ml of previously chilled (-40° C) aqueous ammonia solution (Sigma-Aldrich, Cat. # 32, 014-5) was added, and the mix was shaken until the ammonia started to freeze, creating a well-mixed solid target in the box. The box was then returned to the low temperature freezer and cooled to -130° C.

The targets remained in the freezer until the LGG was ready to fire, and then they were removed and placed in the target chamber which was then evacuated to ~30 mbar. The time taken from removal from the freezer to impact was approx. 20 minutes. In order to

reduce target contamination from carbon-bearing gun debris during the shot, the (impact) target was wrapped in a layer of cling film (~10 μm thick). A blank control target was also placed in the target chamber (out of the direct line of impact) and left uncovered for comparative analysis.

Table 1. LGG shot parameters.

Shot ID	Projectile	Dens. (g cm ⁻³)	Dia. (mm)	Vel. (km s ⁻¹)
G161009#1	SS 304	8.00	1.5	5.75

Preparation of residues: After the shot (Table 1), the impacted target and the control target were removed and placed into a vented oven at a temperature of approximately 90° C, to speed the sublimation/vapourisation of the remnant CO₂ ice and liquid NH₃ and also to decompose the ammonium bicarbonate which is inevitably produced via the reaction: NH₃+H₂O+CO₂→NH₄HCO₃. The water is captured by atmospheric condensation and from the ammonia solution itself. Both targets were left for 12 hours, then the fine powdery residue (coating the bottom and sides of the box) was dissolved in 20 ml of HPLC water (HPLC gradient grade, Fisher Scientific) and filtered through grade 1 filter paper into a washed, sealable, glass container and the water left to evaporate in clean air.

Residue analysis: Residues were analysed with a Jobin Yvon μ-Raman HR640 spectrometer (λ_{laser} = 632.8 nm) and a FTIR spectrometer (Nicolet 380 FT-IR)

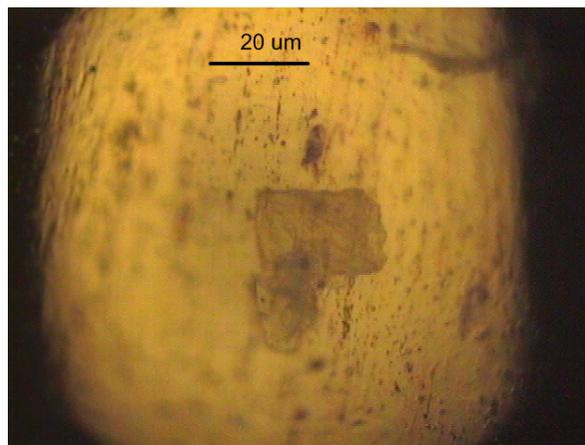


Figure 1: Example of residue grain (on gold substrate) from shot G161009#1

Fig. 1 shows an example of a grain found after washing and filtering the residue. As can be seen, the crystal is irregular and appears to contain smaller (unknown) grains within. It should be noted that several such crystals were found in the residue from G161009#1 but were *NOT* detected in the control residue.

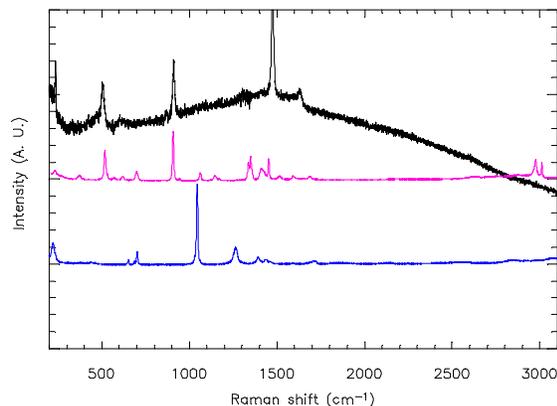


Figure 2. Raman spectrum of crystal from Fig. 1 (upper line-black), pure glycine (middle line-pink), pure ammonium bicarbonate (bottom line-blue).

Table 2: Raman line wavenumbers and relative intensities for pure glycine and the unknown shot residue.

Compound	Raman lines and intensity [†]
Pure glycine (on glass)	504(s), 562(w), 610(w), 689(m), 900(vs), 934(w), 1052(m), 1132(m), 1161(w), 1327(s), 1340(vs), 1400(m,b), 1441(s), 1505(vw), 1584(w), 1677(w), 2966(s), 3003(s)
Residue (on gold)	505(m), 602 (w, b), 689 (vw), 871(w), 901(vs), 981 (vw), 1128 (vw), 1356(w), 1395(vw), 1407(w), 1475(vs), 1512(vw), 1600 (w/vw), 1627(w/m)

[†](vs): very strong, (s): strong, (m): medium, (w): weak, (vw): very weak, (b): broad.

From Fig. 2 (and Table 2) it can be seen that there are *some* matching Raman lines between the residue and pure glycine, but there is also a broad underlying fluorescence in the residue spectrum which may be obscuring some of the less intense lines. There is, however, a better match with the glycine spectra than with the ammonium bicarbonate spectra – which is the most likely contamination.

FTIR analysis was performed by scraping the residue into a pile using a clean spatula and placing it on the diamond anvil stage of the spectrometer. This analysis technique is potentially more ‘destructive’ of our sample than in-situ Raman spectroscopy, simply due to the loss of residue during transfer. Additionally, the method is ‘non-selective’ and will give an FTIR spectrum which is a summation of all the compounds

within the residue. Unfortunately, the very small amount of control target residue made it impossible to obtain a FTIR signal above the background.

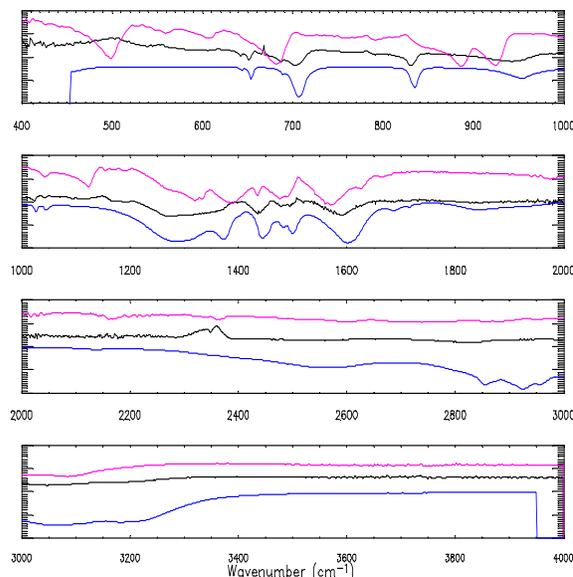


Figure 3. FTIR spectra of residue from G161009#1 (central curve-black). Also shown are the FTIR spectra of pure glycine (upper curve-pink) and ammonium bicarbonate (lower curve-blue).

The FTIR spectra are difficult to accurately interpret, but do seem to suggest a mixture of ammonium bicarbonate and other organic matter (not excluding glycine). The small quantity of residue produced (<1 mg) makes a more accurate determination difficult using our current equipment.

Conclusions: Although more sensitive analytical testing of this type of shock residue is required (and this is ongoing), there are tantalising indications that we have synthesized organic compounds (including, possibly, glycine) by shock impacting a simple ice mixture. This could provide a creation mechanism for prebiotic compounds in the outer solar system. Further experiments are currently underway and time has been obtained on a NMR spectrometer for further analysis.

References: [1] Elsila J. E. (2009) *MAPS*, 44, 1323-1330. [2] Glavin D. P. (2008) *MAPS*, 43, 399-413. [3] Furukawa Y. et al. (2008) *Nature Geoscience*, 2, 62 – 66. [4] Goldman N. I. R et al. (2009) *Proc. of SCCM 2009*. [5] Burchell M. J. et al. (1999) *Meas. Sci. Technol.*, 10, 41-50. [6] Brown R. H. et al., (2006), *Science*, 311, 1425-1428. [7] Verbiscer A. J. et al. (2008), *Bulletin of the American Astronomical Soc.*, 40, 510.

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