

FORMATION AND MOLECULAR EVOLUTION OF ORGANIC SOLIDS UNDER HYDROTHERMAL CONDITIONS IN PLANETESIMAL INTERIORS. G. D. Cody¹, D. Foustoukos¹ and E. Harison¹, ¹Geophysical Laboratory, Carnegie Institution for Science, 5251 Broad Branch Rd., NW, Washington DC (gcody@ciw.edu).

Introduction: Molecular spectroscopic evidence and laboratory experiments provide support for the conjecture that organic solids (IOM) in primitive chondritic meteorites formed in the warm wet interiors of planetesimals [1]. Recently it was noted that the formation of synthetic (syn) IOM generates considerable gas pressure potentially leading to disruptive pressures (exceeding the tensile strength of planetesimals) that could hydrofracture the primitive object [2]. Over the past year detailed kinetic studies of the syn-IOM reaction have been performed in order to better understand both the molecular nature of the reaction and stages of gas generation for the purpose of integrating such kinetics into a thermal evolution model for small planetesimals.

Methods: All reactions were performed using 1.5 ml of de-oxygenated DI water and 170 mg of glucose (C₆H₁₂O₆) charged and flame sealed into glass ampules. Isothermal kinetics were performed over a temperature range from 160 to 250 °C over times of 1 h out to 44 hs. Where solids formed, these were recovered, dried and analyzed for weight yield (mgs) and for molecular structure using ¹³C solid state Nuclear Magnetic Resonance (NMR) spectroscopy. Atomic H/C and O/C ratios were determined using an elemental analyzer interfaced to a mass spectrometer.

Results: The reaction that forms organic solids goes through three stages at a given T and time. First Phase: the initially colorless solutions turn into clear yellow to orange to deep red solutions. Second Phase: there is an abrupt transition where the solutions turn brown and turbid. Third Phase: a black solid precipitate forms leaving a clear yellow solution. Solids are only recoverable from the phase 2 and 3 reaction products.

It was initially proposed that up to 7 independent reactions are required to convert formose sugars into IOM [1]. This implies that resolving the kinetics at the molecular level should be complex which is why ¹³C solid state NMR was employed at the expense of considerable time as at least 50 mg of solids are required to obtain high quality spectra that required multiple reactions at short times to accumulate sufficient solids. What is observed is both simpler than expected (from a kinetic modeling perspective) and more complex from understanding exactly how the reaction occurs. Figure 1 presents a stack plot of ¹³C SSNMR spectra of syn-

IOM formed at 160 °C at times spanning 8-44 hrs.

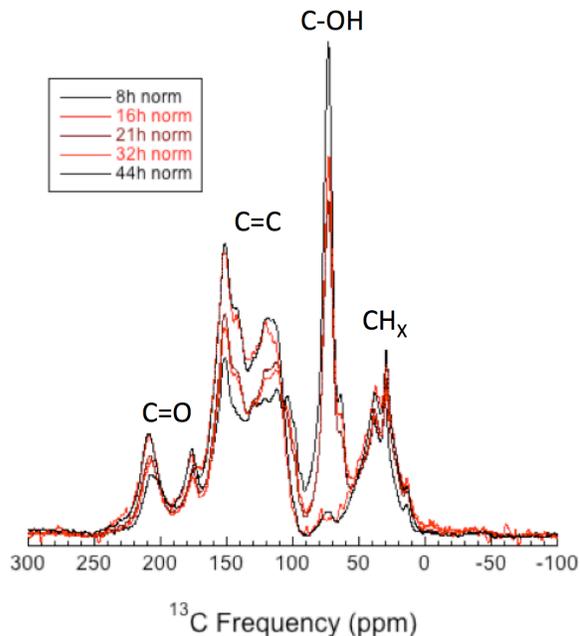


Figure 1: ¹³C SSNMR spectra of syn-IOM synthesized at 160 °C for t=8-44 hrs. Sugars (C-OH) decrease where C=O, C=C, and CH_x moieties grow systematically with loss of sugar moieties (C-OH).

It is immediately clear in Fig. 1 that loss of sugar (C-OH) leads to systematic growth of all other IOM functional groups at nearly equivalent rate. There is no indication of a step-wise evolution through multiple different reactions, rather the net reaction appears to be highly “concerted” (meaning many reactions operating nearly simultaneously). Essentially the reaction appears as CH₂O → IOM, with out any obvious intermediate steps. From a thermo-kinetic modeling perspective these data simplify things even as they complicates verification of any specific reaction mechanism.

Once the black solids precipitate leaving a clear yellow solution (phase 3), molecular structural evolution is much more subtle as is shown in figure 2 for iso thermal reaction of glucose at 250 °C from 1-7 hrs. The most significant molecular evolution observed (once into the black precipitate phase) is the conversion of furan (C=C-O) to simple aromatic (C=C-C) moieties (Fig. 3). This reaction would be required if hydrothermal sugar synthesis of IOM is a valid route to actual chondritic IOM as the furan content of IOM in, e.g., Murchison CM2 is no more than 25 % [1]. Beyond slight growth in COOH, there is no significant change in either C=O or CH_x abundance suggesting

that their synthesis was completely governed by the consumption of CH_2O via the concerted reaction. The conversion of furan to $\text{C}=\text{C}$ (presumably aromatic carbon) is not expected to generate CO_2 or H_2 . The lack of molecular evolution is also evident for $t=32$ and 44hrs at 160°C (Fig. 1). Thus it appears that significant gas generation occurs prior to the formation of black solid precipitation.

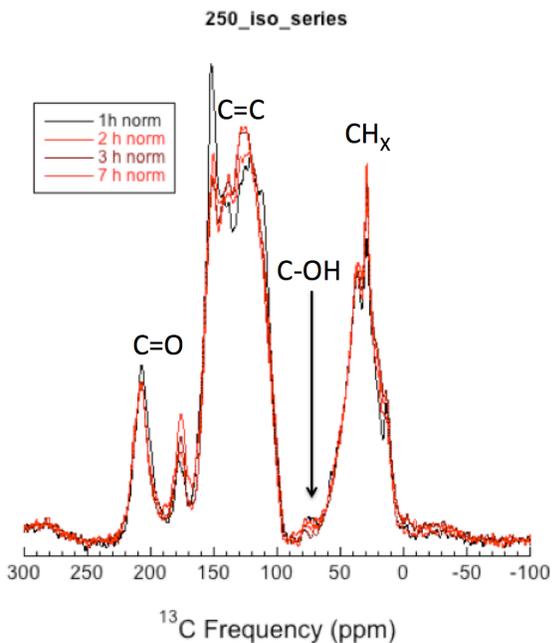


Figure 2: ^{13}C SSNMR of organic solids formed at 250°C $t=1-7$ hrs. All solids appear as black precipitate. Primary molecular evolution involves loss of furan $\text{C}=\text{C}$ (sharp peak at 150 ppm) with growth of $\text{C}=\text{C}$ (at 130 ppm).

One very interesting kinetic feature not immediately obvious in Fig 1 is the discontinuous nature of the syn-IOM reaction. In Fig 3 the evolution in the % of C-OH groups (sugars) as a function of time for reactions at 160, 170, and 180°C respectively. It is apparent that the rate of “C-OH” release is discontinuous through the “turbid solution (TS)” regime and the “black precipitate (BP)” regime. The transition from the TS regime to the BP regime is a phase boundary where syn-IOM solids are no longer soluble in aqueous solution and phase separate into organic precipitate that is the precursor of what is proposed to be chondritic IOM. In the context of understanding the rate and nature of gas pressure generation, these data suggest that most gas generation occurs during Phase 2 (TS).

The critical first reaction involves dehydration of sugars leading to the formation of chains of ketones and ultimately furans. This can be written as



At 180°C after 24 hours one collects 52 mgs of solids with a measured composition of $\text{CH}_{0.78}\text{O}_{0.25}$ which indicates considerable gas generation: the overall reaction being:

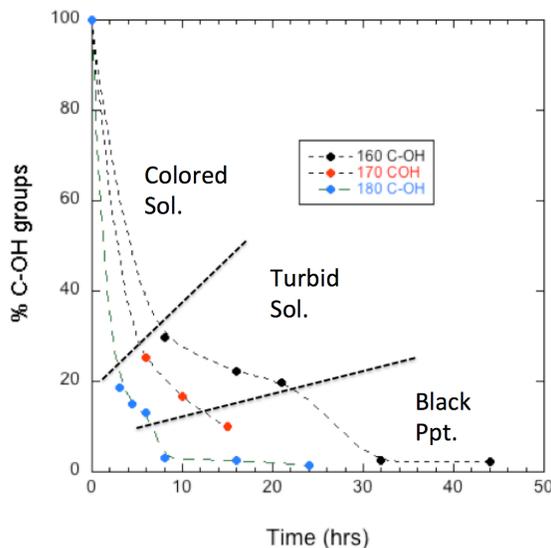
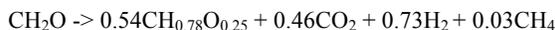


Figure 3: The concentration of C-OH groups as detected via ^{13}C SSNMR as a function of T and time. There are three regimes observed, 1) colored clear solutions, 2) opaque turbid solutions (TS), and black precipitate (BP) in colored clear solutions. Solids are recovered only from TS and BP phases.

From the discussion above it appears that the vast majority of gas generation occurs during phase 2. Rapid gas generation over a shorter time interval will be much more disruptive than slow gas generation over a long interval. These studies are being used to derive thermo-kinetic data to model hydrothermal synthesis during planetesimal thermal evolution arising from radiogenic heating. cursory analysis of the CH_2O loss rates in phase two yields an apparent activation energy (E_A) on the order of 20.3 kJ with an exponential factor, A, of 8.6×10^5 secs. This a relatively low value for E_A relative to kerogen maturation, oil and gas generation values which are typically in the range of 200 kJ [3]

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References: [1] Cody G. C et al. (2011) *PNAS* 108, 19171. [2] Cody G. D., Foustoukos D., Bullock (2019) *LPS LI*, Abstract #2692 I. J. (2002) *LPS XXXIII*, Abstract #1402. [3] Braun R. L., Burnham A. K. (1987) *Energy & Fuels*, 1, 153-161.