



A kinetic study of the formation of organic solids from formaldehyde: Implications for the origin of extraterrestrial organic solids in primitive Solar System objects



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ABSTRACT

Aqueous organic solid formation from formaldehyde via the formose reaction and subsequent reactions is a possible candidate for the origin of complex primitive chondritic insoluble organic matter (IOM) and refractory carbon in comets. The rate of formation of organic solids from formaldehyde was studied as a function of temperature and time, with and without ammonia, in order to derive kinetic expressions for polymer yield. The evolution in molecular structure as a function of time and temperature was studied using infrared spectroscopy. Using these kinetic expressions, the yield of organic solids is estimated for extended time and temperature ranges. For example, the half-life for organic solid formation is ~ 5 days at 373 K, ~ 200 days at 323 K, and ~ 70 years at 273 K with ammonia, and ~ 25 days at 373 K, ~ 13 years at 323 K, and $\sim 2 \times 10^4$ years at 273 K without ammonia. These results indicate that organic solids could form during the aqueous alteration in meteorite parent bodies. If liquid water existed early in the interiors of Kuiper belt objects (KBOs), formaldehyde could convert into organic solids at temperatures close to 273 K, and possibly even below 273 K in the ammonia–water system.

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1. Introduction

The origin of insoluble organic matter (IOM) in primitive meteorites has been a long standing astrochemical question and over the past fifty years a variety of potential synthesis mechanisms have been proposed. These include proposals for organic solids formation in hot inner proto planetary nebula (e.g., Anders et al., 1973; Sagan and Khare, 1979; Morgan et al., 1991; Llorca and Casanova, 2000; Nuth et al., 2008; Saito and Kimura, 2009), and proposals for organic solids synthesis in the cold interstellar medium or outer solar nebula (e.g., Greenberg et al., 1995; Bernstein et al., 2003; Charnley and Rodgers, 2008; Herbst and van Dishoeck, 2009; Ciesla and Sandford, 2012). Alternatively, the formation of organic solids that constitute IOM in chondrites has been proposed to have occurred in the circumstellar environments surrounding highly evolved stars (e.g., Kwok and Zhang, 2011). In either hot or cold synthesis proposals, all such proposals favor IOM forming prior to chondritic parent body accretion.

An alternative scenario that has recently been proposed is the possibility that carbonaceous solids formed from reactions that

occurred, post-accretion, in the warm wet interiors of planetesimals (Cody et al., 2011; Kebukawa et al., 2013). In addition to organic solids, the very considerable molecular complexity exhibited in the suite of soluble compounds extracted from the Murchison meteorite has lead others to suggest that complex organic synthesis likely occurred post accretion, within the meteorite parent body (Schmitt-Kopplin et al., 2010; Cooper et al., 2011). Given the extensive organic chemistry that could have occurred within chondritic parent body interiors, the possibility for the formation of organic solids also appears plausible. Cooper et al. (2001) had previously identified low molecular weight sugar and sugar-related compounds (polyalcohols) in aqueous extracts from the Murchison meteorite and speculated that these compounds were plausibly derived from interstellar formaldehyde via the formose condensation reaction within the meteorite parent body, i.e., the formose reaction that involves formaldehyde condensing to yield glycolaldehyde, glycolaldehyde condensing with formaldehyde to yield glyceraldehyde, and so on into larger sugar molecules (Boutlerow, 1861; Breslow, 1959; Shapiro, 1988; Ricardo et al., 2004; Cody et al., 2011; Kopetzki and Antonietti, 2011). Cooper et al. (2001) also speculated that chondritic IOM might also be the polymerized end product of the formose and other reactions. Astronomers have also proposed that the formose reaction was a likely source for interstellar glycolaldehyde detected in the

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Galactic center source Sagittarius B2(N) and a hot molecular core, G31.41+0.31 (Hollis et al., 2000; Halfen et al., 2006; Beltrán et al., 2009). A recent detection of glycolaldehyde has been reported in a solar-type protostar, where a gas–grain formation mechanism was proposed (Jørgensen et al., 2012). Therefore, both formaldehyde and glycolaldehyde are expected to be present in the icy mantles of dust grains that ultimately coalesced into planetesimals.

Cody et al. (2011), using multi-dimensional solid-state nuclear magnetic resonance (NMR) spectroscopy, showed that furan moieties are a major constituent of IOM (from the carbonaceous chondrite, Murchison, a CM2) and suggested that such furanic moieties most likely formed from sugars. Cody et al. (2011) then tested whether organic solids formed through formaldehyde polymerization and other reactions were similar at the molecular level to primitive extraterrestrial organic solids using molecular spectroscopy (both NMR and carbon X-ray absorption near edge structure, C-XANES, spectroscopy). Cody et al. (2011) revealed that the molecular structure of the organic solids formed from formaldehyde was very similar at the functional group level to primitive chondritic IOM, organic solids present in both hydrated and anhydrous IDPs, and also organic solids in particles collected from Comet 81P/Wild 2 (Sandford et al., 2006; Cody et al., 2008a). Significantly, these results suggest that the major organic reservoirs in both primitive chondrites and comets were derived from a common molecular precursor and formed through similar reaction pathways. However, if the condensation of formaldehyde derived sugars was the route to the synthesis of IOM, then the implication is that IOM formed after planetesimal formation, within planetesimal interiors in the presence of aqueous fluids. Comets and anhydrous IDPs, understood to be derived from comets, originated from the outer Solar System, either from the Kuiper belt or the Oort cloud. The possibility of liquid water in these outer Solar System objects presently is unlikely, although during planetesimal collisions there may be sufficient kinetic energy to create temporarily wet domains in the interiors of planetesimal fragments. The possibility that liquid water existed in the deep interiors of large Kuiper belt objects (KBOs) early in Solar System history may have been possible (Brown, 2012). Recently, evidence for low-temperature aqueous processing in a KBO was found in the Comet 81P/Wild 2 dust particles, as revealed by characteristic sulfide mineral assemblages that plausibly form through aqueous reaction (Berger et al., 2011). However, hydrous phyllosilicate phases, the most common aqueous alteration products in chondrites and hydrated IDPs, have not yet been identified in the Comet 81P/Wild 2 samples (Brownlee et al., 2012).

Liquid water could have existed in the interiors of large KBOs early in Solar System history where heating derived from the decay of radiogenic elements could have heated cores to temperatures up to or exceeding 273 K. It has been shown that amorphous silicates within anhydrous IDPs (considered to be of cometary origin) are very susceptible to aqueous alteration and transform into hydrated silicates in the presence of liquid water (Nakamura-Messenger et al., 2011), although in this particular study no determination of the kinetics of such transformations was performed. However, it has also been reported that hydrous silicates can be found in so-called ‘anhydrous’ IDPs (Nakamura et al., 2005); implying at least some degree of aqueous history and processing.

More recently, the formation of organic solids from formaldehyde was studied in more detail, focusing on the relationship between synthesis temperature and resultant molecular structure and included a study of the presence of ammonia in the chemical system (Kebukawa et al., 2013). It was found that addition of ammonia to the solution enhances the polymerization reaction at lower temperatures (Kebukawa et al., 2013). However the laboratory synthesis experiments were conducted isothermally at

temperatures spanning 363–523 K for a fixed time period, 3 days (Kebukawa et al., 2013). More realistic reaction conditions for planetesimal interiors are temperatures closer to 273 K and much longer durations (many years). Detailed kinetic data provide an efficient way to apply laboratory scale experiments to estimate chemical transformation at more relevant cosmochemical timescales (e.g., Nelson et al., 1987; Kebukawa et al., 2010). Here we report the organic solids formation kinetics from condensation of formaldehyde and subsequent reactions, in order to constrain the time and temperature necessary to form organic solids in planetesimal interiors, and we then compare these timescales to those required for hydrated silicate formation. In this paper, the focus is on the kinetics of the organic solid yield rather than molecular structure and proposed reaction mechanisms, which have been discussed in detail in previous papers (Cody et al., 2011; Kebukawa et al., 2013).

2. Experimental procedures

2.1. Synthesis of organic solids from formaldehyde

Organic solids from formaldehyde were synthesized at various temperatures and times, in order to obtain the kinetic parameters for solid yield. The detailed description of the organic solids synthesis method is found in Kebukawa et al. (2013), the protocol is based on the one in Ricardo et al. (2004) and Cody et al. (2011). The starting solution contained pure formaldehyde in the form of paraformaldehyde at 4 mmol (120 mg) and glycolaldehyde 2 mmol (120 mg), Ca(OH)₂ (30 mg; given the low solubility in water, Ca(OH)₂ exists largely as a solid), and deionized water (2 ml). Ammonia was added to the system as 14.8 N NH₄OH (54 μl providing an N/C atomic ratio = 0.1). Glycolaldehyde is used as an initiator (see Kopetzki and Antonietti (2011) and references there in) and works to place the formose reaction kinetically in the steady state regime as opposed to the autocatalytic regime. Paraformaldehyde and glycolaldehyde (dimer) were obtained from Sigma-Aldrich. Calcium hydroxide (Ca(OH)₂) and ammonium hydroxide are obtained from Fisher Scientific. Paraformaldehyde hydrolyzes very rapidly at high pH to yield pure formaldehyde. Ca(OH)₂ was added in order to make the starting solution with a pH in the range of 11.5–11.7, and Ca(OH)₂ also acts as a catalyst of the formose reaction (Ricardo et al., 2004; Cody et al., 2011; Kopetzki and Antonietti, 2011). Each solution charged into glass tubes that were flame sealed and then heated isothermally from 363 K up to 523 K over reaction periods spanning from 1 h to 264 h (11 days). After the heating, the supernatant is removed and the black solid is washed with 2 N HCl to remove bound calcium ions. The solids were then washed with deionized water several times until solution pH becomes neutral, and dried under mild heating (<353 K) for several hours.

2.2. Fourier transform infrared (FTIR) micro-spectroscopy

In order to evaluate molecular structural evolution of the organic solids derived from formaldehyde that occur as a function of the heating time and temperature, the organic solids were analyzed using Fourier transform infrared (FTIR) micro-spectroscopy. The small amount of the formaldehyde polymer was pressed onto a KBr plate freshly cleaved from ~5 × 5 × 5 mm³ cube. Infrared absorption spectra were collected using a Fourier transform infrared micro-spectrometer (Micro FTIR; Jasco FT/IR-6300 + IMV4000) with a ceramic infrared light source, a germanium coated KBr beam splitter, a mercury–cadmium–telluride (MCT) detector, and 16× Cassegrainian mirrors. During analysis, the microscope and the FTIR were continuously purged with dry N₂, beyond this no

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