

A NOTE ON THE PREBIOTIC SYNTHESIS OF ORGANIC ACIDS IN CARBONACEOUS METEORITIES

JOHN F. KERRIDGE

Institute of Geophysics, University of California, Los Angeles CA 90024-1567, U.S.A.

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Abstract. Strong similarities between monocarboxylic and hydroxycarboxylic acids in the Murchison meteorite suggest corresponding similarities in their origins. However, various lines of evidence apparently implicate quite different precursor compounds in the synthesis of the different acids. These seeming inconsistencies can be resolved by postulating that the apparent precursors also share a related origin. Pervasive D enrichment indicates that this origin was in a presolar molecular cloud. The organic acids themselves were probably synthesised in an aqueous environment on an asteroidal parent body, the hydroxy (and amino) acids by means of the Strecker cyanohydrin reaction.

Introduction

Carbonaceous chondrites, exemplified by the Murchison CM2 meteorite, contain significant quantities of a variety of organic acids. These include homologous series of monocarboxylic (hereafter carboxylic, hydroxycarboxylic (hereafter hydroxy) and amino acids (e.g., Cronin *et al.*, 1988). Several features of the relative abundances and isotopic compositions of these acids have been interpreted in terms of possible prebiotic mechanisms of organic synthesis that might have been responsible for, or contributed to, the observed meteoritic populations. It is the purpose of this note to show, first, that some of these lines of inquiry are in apparent conflict with each other and, second, that resolution of that conflict will probably shed considerable light on the pathways and environments of organic synthesis in the early solar system.

Carboxylic Acids: Evidence from Carbon and Hydrogen Isotopes

Murchison contains a population of carboxylic acids that shares, like most other well-characterised families of organic molecules in Murchison, the following features: Essentially complete structural diversity; a predominance of branched over straight-chain species; and a systematic decrease in abundance with increasing carbon number in homologous series (e.g., Cronin *et al.*, 1988). In addition, for the series C₂ through C₅, i.e., acetic through valeric acids, Yuen *et al.* (1984) showed that the ¹³C/¹²C ratio decreased systematically with increasing carbon number, Figure 1. Furthermore, they showed that the same phenomenon can be observed for the light alkanes, from methane through pentane, Figure 1. Yuen *et al.* (1984) concluded that their results point strongly towards synthesis of these compounds by a process that involves kinetically controlled formation of higher-molecular-weight species from lower homologues. They also pointed out that the parallel isotopic variation between

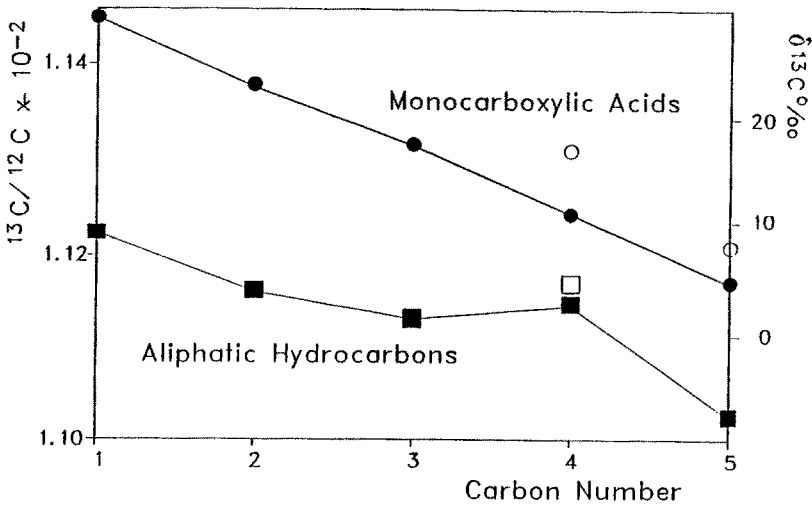


Fig. 1. $^{13}\text{C}/^{12}\text{C}$ ratios for individual aliphatic hydrocarbons and carboxylic acids, extracted from the Murchison meteorite, plotted against C number. For example, 1 denote methane or CO_2 , 2 ethane or acetic acid, and so forth. Values for branched isomers are indicated by open symbols. Isotope ratios also expressed in the delta notation as deviation in parts per thousand relative to the terrestrial standard, PDB. After Yuen *et al.* (1984).

alkanes and carboxylic acids 'implies that some aspects of their histories are similar'.

An implication of the data in Figure 1, recognised by Yuen *et al.* (1984), is that the aliphatic carbon in a carboxylic acid is likely to be isotopically similar to that in the corresponding alkane whereas the carboxyl carbon probably resembles that in CO_2 . If true, this would point towards either derivation of the aliphatic group from the corresponding alkane (and the carboxyl group from the CO_2) or derivation of both aliphatic and alkane carbon from a common precursor (and similarly for carboxyl and CO_2 carbon). This point will be discussed further below.

The isotopic composition of hydrogen in meteoritic carboxylic acids is known in less detail than is the case for carbon, but the single measurement in the literature is of considerable significance. Epstein *et al.* (1987) derived a δD value of +377‰ for a bulk carboxylic acid fraction from Murchison. This value is almost certainly a lower limit to the true indigenous value, partly because of hydrogen-isotope exchange with laboratory reagents and/or water on the Murchison parent body, and partly because of terrestrial contamination, to which even Murchison is not immune (e.g., Cronin and Pizzarello, 1990). The true value is not presently calculable but may well be comparable to those measured for the meteoritic kerogen-like fraction (e.g., Robert and Epstein, 1982; Kerridge, 1983) and amino acids (Epstein *et al.*, 1987), i.e., of the order of +1000‰. The significance of such D enrichment will be discussed later.

similar structures.) Thus, the measured $\delta^{13}\text{C}$ and δD values for the amino acids [Epstein *et al.*, 1987] can be, at least tentatively, attributed also to the hydroxy acids. Those values are +23.1 and +1370‰, respectively.

Note also in Figure 2 that the individual atoms in the resulting acids can be traced back to specific starting compounds. Thus, the aliphatic carbon in glycolic acid, or glycine, is derived from formaldehyde and the carboxyl carbon from HCN. The situation is somewhat more complicated for hydrogen because of additional contributions from water and ammonia, plus the relative ease with which the hydrogen isotopes exchange between different molecules. However, it seems likely that the aliphatic hydrogen would be derived from the formaldehyde.

Comparison of Carboxylic and Hydroxy Acids

In Figure 3, the most abundant carboxylic acid, acetic, is compared with its hydroxy-acid counterpart, glycolic acid. The structural similarity is immediately apparent. Furthermore, the carbon isotopic composition of the acetic acid, +22.7‰ (Yuen *et al.*, 1984), is closely similar to that measured for glycine, +22‰ (M. H. Engel *et al.*, 1990), and therefore inferred for glycolic acid.

The central hypothesis of this note is therefore that the carboxylic and hydroxy acids in Murchison are sufficiently similar to suggest that they likely share some common history, and that by combining what we currently know about each individual history, we can define more closely the mechanism(s) and environment(s)

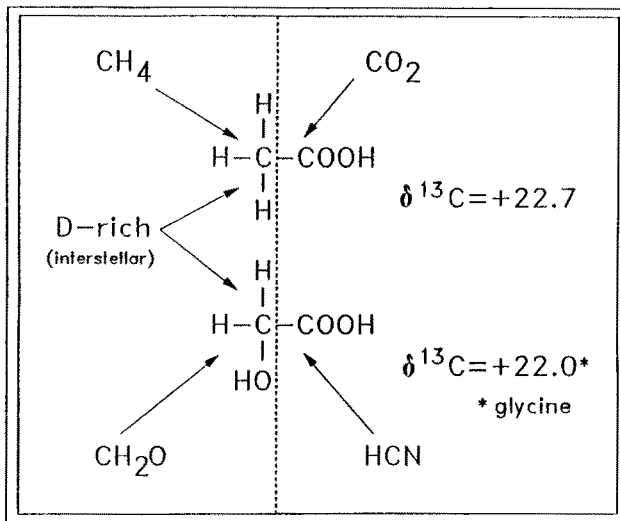


Fig. 3. Comparison of some of the measured or inferred properties of acetic acid (top) and glycolic acid (bottom) extracted from the Murchison meteorite. The molecules connected by arrows to the two acids are believed either to be precursors of, or to share a common history with, the appropriate functional groups in the organic acids. Note that the isotopic properties of the glycolic acid are inferred from those of the corresponding amino acid, glycine.

responsible for synthesis of meteoritic organic acids and, in particular, the nature of their precursor material.

Significance of D Enrichments

The discovery of large D enrichments in meteoritic organic matter led immediately to the recognition that such dramatic isotope fractionation could not reasonably have been generated in the early solar system, and that incorporation of interstellar molecules was the most plausible explanation for the meteoritic data (e.g., Kolodny *et al.*, 1980; Geiss and Reeves 1981; Robert and Epstein, 1982). (It is well known that hydrogen-bearing molecules in dense interstellar clouds are highly enriched in deuterium, resulting from the strong isotopic fractionation that accompanies ion-molecule reactions taking place at the very low temperatures characteristic of such clouds, 10 to 100 K (e.g. Wannier, 1980).) This view has been occasionally criticised (Halbout *et al.*, 1990) but is generally accepted (e.g., Anders, 1986; Mullie and Reise, 1987; Cronin *et al.*, 1988; Zinner, 1988). However, the nature of the putative interstellar carrier phase(s) is not at all understood, possibilities ranging from incorporation of intact surviving interstellar molecules to *de novo* organic synthesis from H₂ 'contaminated' with hydrogen derived from interstellar material. In particular, both Epstein *et al.* (1987) and Cronin *et al.* (1988) considered the question of whether the meteoritic amino (and carboxylic) acids were themselves interstellar molecules or whether they were synthesised in the solar system from interstellar precursors. Cronin *et al.* (1988) pointed out that the precursors to Strecker synthesis of amino acids were all well-known interstellar molecules. Here we explore further the implications of postulating such interstellar precursors for meteoritic organic acids, specifically considering the role that carbon-isotopic data can play in constraining such scenarios.

Constraints on the Origin of Organic Acids in Meteorites

Summarising the relevant observations described above, we can identify the following key factors. First, the aliphatic carbon in carboxylic acids is apparently closely related to that in the corresponding alkanes. Second, the aliphatic carbon in glycolic and other hydroxy acids, despite the fact that they seem to be closely related to acetic and other carboxylic acids, was apparently derived from formaldehyde and other aldehydes (and ketones, which probably also contributed to the Strecker synthesis). Third, organic-acid synthesis likely took place in an aqueous environment on one or more asteroids, that served as parent bodies for Murchison and other carbonaceous chondrites. Fourth, aliphatic hydrogen in carboxylic and hydroxy acids was probably derived, at least in part, from interstellar molecules that escaped homogenisation with the major reservoir of solar-system hydrogen, H₂ gas. How can these different conclusions be reconciled?

A trivial explanation would be that aldehydes were synthesised in the early solar

system from alkanes of interstellar origin, but there are several problems with this scenario, notably the lack of a relatively straightforward reaction pathway from, say, methane to formaldehyde. Furthermore, thermochemical calculations show that aldehydes would not have been stable in a nebula of solar composition (e.g., Fegley and Prinn, 1989), though conceivably this would not rule out their production in some microenvironment in the early solar system, decoupled from the nebular gas. (Such a microenvironment has been identified by Fegley and Prinn (1989) in the form of subnebulae around the giant planets. However, it seems unlikely that organic matter synthesised in such a subnebula could escape from the gravitational well of its giant planet, to permit incorporation into an asteroid.) Methane itself could plausibly have been produced by catalysed hydrogenation of CO in the solar nebula (e.g., S. Engel *et al.*, 1990), but production of the full suite of Murchison alkanes by such a mechanism is problematical. Such a catalytic synthesis would be expected to be structurally selective (Hayatsu and Anders, 1981), whereas the structural diversity of the Murchison alkanes argues against production by a catalytic process (Cronin and Pizzarello, 1990). On balance, production of aldehydes from alkanes in the early solar system seems improbable. The inverse reaction is considered below and shown to be inconsistent with observation, leading to the conclusion that aldehydes and alkanes probably shared a common origin rather than one being derived from the other. Could this common origin have been in an interstellar cloud?

Formaldehyde is well known as a relatively abundant interstellar molecule, but the possible existence of interstellar alkanes can only be inferred, as they lack suitable spectral signatures. Nonetheless, the presence of alkanes in molecular clouds seems plausible (Irvine *et al.*, 1989). Whether they would survive the collapse phase and formation of the solar nebula is problematical, however, given their volatility. The implications of identifying the Murchison alkanes with interstellar molecules will be explored below. Meanwhile, we outline a sequence of events that seems to be consistent with the available evidence.

The Murchison parent asteroid accreted a variety of materials including water ice condensed below about 200 K in the solar nebula, and a suite of interstellar organic compounds, some of which may have been preserved in polymerised form as a result of cosmic-ray irradiation [Greenberg 1982]. (Polymerised formaldehyde has been proposed as a major organic constituent of the nucleus of comet Halley (Huebner *et al.*, 1989).) The water ice would have had a D/H ratio in the region of 8×10^{-5} ($\delta D = -500\text{‰}$), corresponding to equilibrium exchange at the quench temperature for H_2-CH_4 of 560 K (Grinspoon and Lewis, 1987), whereas the interstellar organics would have had D/H ratios possibly ranging up as high as 0.1 ($\delta D = +600\text{‰}$) (e.g., Snell and Wootten, 1979). Evidence from meteorites (e.g., Hewins and Newsom, 1988; McSween *et al.*, 1988) shows that many, perhaps all, asteroid-sized objects in the inner solar system were subject to internal heating very early in their history. Possible heat sources included decay of now-extinct ^{26}Al (Lee *et al.*, 1977) and electromagnetic induction driven by the intense early

solar wind (Herbert and Sonett 1978).

In objects that accreted at sufficiently low temperatures to have incorporated water ice, the early heating would first have melted that ice, mobilising water as either liquid or vapor. That water would have diffused to the surface, probably forming a relatively durable 'permafrost' layer (DuFresne and Anders, 1962), beneath which chemically active liquid water could have been trapped for long enough to alter the initially anhydrous silicate minerals to the secondary, phyllosilicate-dominated lithology now observed in carbonaceous chondrites (e.g., Kerridge and Bunch, 1979; Zolensky and McSween, 1988). Because the active water would have been derived predominantly from the relatively D-poor ice, the resulting phyllosilicates would have relatively low D/H ratios, as is observed for carbonaceous chondrites (e.g., Robert and Epstein, 1982).

In addition to free water, organic molecules would have been liberated during heating of the asteroid interior, partly by evaporation and partly by pyrolytic degradation of more complex compounds. Reconsideration of evaporated species in cooler parts of the asteroid would have generated the supply of aldehydes, as well as ketones, cyanide and ammonia, needed to drive the Strecker synthesis in the aqueous near-surface regions. At first sight, the meteoritic alkanes seem to be plausible pyrolytic-degradation products, thus possibly providing a genetic link between them and the aldehydes, but such an origin would not explain the carbon-isotope data of Yuen *et al.* (1984): those data point strongly towards formation of higher alkane homologues from smaller ones rather than production of simple compounds by breakdown of more complex ones. These data therefore suggest that the alkane population predated accretion of the Murchison asteroid, by synthesis in either the solar nebula or the presolar interstellar cloud. Which of those environments represents the more likely region for alkane formation is an issue beyond the scope of this study, but we note that previous evidence for Fischer-Tropsch synthesis of meteoritic alkanes in the solar nebula (e.g., Hayatsu and Anders, 1981) has recently been called into question (Cronin and Pizzarello, 1990). Wherever alkanes were produced, however, it seems that some of them were ultimately trapped in the low-temperature, asteroid-surface lithology that eventually became the Murchison meteorite.

Discussion

A scenario in which presolar aldehydes, ketones, cyanide and ammonia reacted in the aqueous near-surface regions of an asteroid to produce a mixture of carboxylic, hydroxy and amino acids appears broadly consistent with the chemical and isotopic data for Murchison (see also Cronin *et al.*, 1988), but several points require further clarification. Some are susceptible to experimental investigation but others will likely remain in the realm of conjecture.

Clearly, the various isotopic compositions that have been inferred here, i.e., carbon and hydrogen isotopes in hydroxy acids in general and glycolic acid in particular,

need to be directly measured, preferably using an approach that permits discrimination between aliphatic and carboxyl groups. More generally, such information, including the isotopic composition of nitrogen and oxygen, is desirable for a whole range of organic compounds in meteorites, such as individual amino acids and hydrocarbons, as well as any ammonium salts that can be extracted from Murchison. (We have assumed above that the ammonia participating in the Strecker synthesis was of interstellar origin, because of thermochemical arguments against significant ammonia production in the solar nebula (e.g., S. Engel *et al.*, 1990). The isotopic composition of any residual ammonia might resolve that issue. Isotope exchange during the period of aqueous activity probably rules out straightforward use of the hydrogen isotopes, but the nitrogen isotopes might provide indirect evidence. A hint of a systematic relationship between D/H and $^{15}\text{N}/^{14}\text{N}$ is apparent in bulk data (Kerridge, 1985) and if such a relationship is confirmed by future, more refined studies, it might prove possible to use the nitrogen-isotopic composition to infer the former D/H ratio of the ammonia.)

Considerable uncertainty surrounds the question of survival of interstellar molecules, particularly the volatile alkanes such as methane, so that they could have been incorporated intact into solid solarsystem objects. Although the high level of deuteration of several organic species in meteorites is strong evidence for survival of some kind of interstellar material, the actual nature of the D-rich carrier phase is not yet known, as noted earlier. Eventually, knowledge of the detailed distribution of deuterium between different molecules should at least partly resolve this issue, as interstellar and solarsystem reaction pathways are unlikely to be characterised by the same isotopic fractionation patterns. Meanwhile, however, we have to assume that the requisite interstellar species survived to participate in the Strecker synthesis.

An issue implicit in our discussion of the interstellar deuterium signature above, is the question of a possible interstellar carbon-isotope signature. Is the observed distribution of carbon isotopes in Murchison organic matter consistent with preservation of some interstellar molecules? There are two aspects to this question, involving respectively the match between the normal solar-system $^{13}\text{C}/^{12}\text{C}$ ratio (0.0112) and those measured in Murchison, and the intramolecular distribution of ^{13}C in Murchison.

Except for trace constituents such as silicon carbide and graphite of circumstellar origin (Anders, 1988; Amari *et al.*, 1990), carbon isotope ratios measured in Murchison fall within the range observed for terrestrial materials, in striking contrast to the large differences observed for D/H ratios. Part of this discrepancy can be attributed to the inherently smaller fractionation factors for carbon *vis-à-vis* hydrogen but ion-molecule reactions in interstellar clouds are nonetheless capable of fractionating carbon isotopes by a factor of two (Watson, 1976) and it is not clear whether dilution by locally produced material would have totally eliminated such an interstellar signature in carbon. Among existing data for meteoritic organics, not only are the $^{13}\text{C}/^{12}\text{C}$ ratios normal for solar-system material, but there is no detectable correlation between variations in that ratio and those in D/H, suggesting

that in general carbon and hydrogen isotopic systems are decoupled from each other. This would argue in favor of extensive reprocessing within the solar system and against large-scale preservation of intact interstellar molecules. However, it seems premature to extend this generalisation to individual families of compounds for which suitably detailed isotopic data do not yet exist.

Focusing on the Murchison alkanes, for which hydrogen-isotope data are not yet available, the observed lack of a dramatic fractionation in their carbon isotopes relative to 'normal' solar-system carbon cannot therefore be used to rule out an interstellar origin. Similarly, the systematic variation in $^{13}\text{C}/^{12}\text{C}$ ratio with carbon number observed by Yuen *et al.* (1984), though modest compared with fractionations observed among many carbon species in ion-molecule reactions (e.g., Smith and Adams, 1980), cannot be regarded as inconsistent with an interstellar origin without more knowledge of the putative ion-molecule reaction pathways responsible for alkane synthesis.

We note, however, that somewhat more information may be available with regard to the carboxyl carbon and its possible precursor(s). As mentioned above, within the context of the Strecker synthesis the carboxyl carbon in the hydroxy and amino acids is derived from HCN. We have no direct information on the $^{13}\text{C}/^{12}\text{C}$ ratio of cyanide in Murchison, but that ratio has been measured for CN in the coma of comet Halley, yielding a value of 0.0159 ± 0.002 (Wyckoff and Lindholm, 1989), though a more recent analysis of the data (Kleine *et al.*, 1990) suggests a value closer to, and possibly indistinguishable from the average solar-system value of 0.0112. The lower value poses no problem for the scenario considered here, but if Halley HCN, believed to be the principal parent molecule for CN (Wyckoff *et al.*, 1989), is representative of HCN in the early solar system, the higher value would lead to substantial ^{13}C enrichment in carboxyl carbon derived therefrom. As noted above, carboxyl carbon in Murchison acetic acid is enriched in ^{13}C but only to $^{13}\text{C}/^{12}\text{C} = 0.0116$ ($\delta^{13}\text{C} = 35\text{‰}$), far less than would be anticipated on the basis of the Halley data. However, there are good grounds for questioning the extrapolation of the Halley data to solar-system material in general. Production of HCN by known ion-molecule pathways tends to favor ^{12}C , so that the carbon reservoir from which the Halley HCN was presumably derived would have been even more enriched in ^{13}C than the measured CN value. But in such a case, it would have been virtually impossible to derive normal solar-system carbon from such a reservoir. It therefore seems most likely that, if the higher $^{13}\text{C}/^{12}\text{C}$ ratio is correct, the carbon in Halley is anomalous, possibly for nucleosynthetic reasons, with respect to mean solar-system composition, as suggested by Wyckoff and Lindholm [1989], but this issue needs much further study.

Conclusions

Some of the chemical and isotopic features of the organic acids in the Murchison meteorite are not explicitly predicted by the model outlined above, but none appear

to be inconsistent with such a model at this time. We therefore conclude that a model in which aldehydes, ketones, cyanide and ammonia, of partly or wholly interstellar origin, react to produce organic acids in an aqueous asteroidal environment, deserves serious consideration.

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