



Carboxylic Acid Abundances in the Tagish Lake Meteorite: Lithological Differences and Implications for Formic Acid Abundances in Carbonaceous Chondrites



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Introduction

The most abundant soluble organic compounds in carbonaceous chondrites are typically carboxylic acids [1]. The most abundant monocarboxylic acid in interstellar space is formic acid [e.g. 2,3]. It is generally accepted that the organic material in carbonaceous chondrites such as the Tagish Lake meteorite is derived from interstellar or nebular sources [4,5]. It is somewhat surprising, therefore, that so far only what have been described as small or moderate formic acid concentrations have been found in aqueous extracts of carbonaceous chondrites [6-11]. Previous reports have ascribed the unexpectedly low formic acid abundances to either compound loss during extraction and subsequent work up, or to depletion caused by environmental processes, such as evaporation and/or aqueous leaching of the compound from the meteorite upon its exposure to the Earth's hydrosphere [6,7]. Here we present our analysis of the water-soluble monocarboxylic acids in three different lithologies within the Tagish Lake meteorite using SPME-GCMS and SPME-GCIRMS procedures recently developed by [6]. Our results conclusively show that formic acid is, by a wide margin, the most abundant monocarboxylic acid in all of the Tagish Lake lithologies investigated so far. This is in stark contrast to all previous studies in which it was concluded that the formic acid concentration was the lowest or one of the lowest of those monocarboxylic acids present in the extract [6-11]. Moreover, our serendipitous realization that formic acid has a very low response factor when run on either GCMS (quadrupole) or GC-FID [12] instruments suggests that previous studies on carbonaceous chondrites may have dramatically underestimated the quantities of formic acid present. Also, a close inspection of the formic acid to acetic acid ratios for (11i) and (11v) has led us to conclude that the overall oxidation levels for the water soluble organics from the two lithologies are different.

Methods/Materials

Three samples were analyzed: Sample (11v) consists of disaggregated material composed of chondrules set in a fine-grained matrix of phyllosilicates, sulfides and abundant magnetite. It appears to be most similar to the carbonate-poor lithology of [13]. GCMS analysis of DCM extracts of this lithology were found to be relatively rich in reduced organics such as long-chain hydrocarbons, PAHs and alkyl-substituted benzenes. Sample (11i) is an example of a "dark, dusty" lithology consisting almost entirely of fine-grained (<5 µm) material typical of matrix (incl. phyllosilicates, magnetite, and sulfides). Reduced organics are far more scarce in (11i). Sample (5B) is compact, coherent lithology similar to (11i) in its composition. Only trace quantities of reduced organics are present in this lithology. In a typical extraction, a crushed ~0.70 g-subsample of a particular lithology in ca. 20 mL H₂O was heated at reflux (100°C) for 6 h. The pH of the colorless filtrate was increased to ~11 via the addition of 4 drops of ultrapure 6 M NaOH(aq) (this step converts all carboxylic acids present into their corresponding, non-volatile carboxylate salts). The volume of the filtrate was reduced to ~1 mL on a rotary evaporator operating at 75°C. In order to regenerate the acids, the pH of the concentrate was pushed below 2 by the addition of 4 drops of ultrapure 6 M HCl(aq). The concentrated water extracts were analyzed by sorption of the monocarboxylic acids on an SPME (solid phase microextraction) fiber coated with PEG (polyethylene glycol), followed by gas chromatography with mass spectrometry (GCMS). The acids were flashed off the fiber in the hot GC port, separated on a Nukol column and finally, determined with an Agilent Technologies 5975-C GC-MS quadrupole detector. The monocarboxylic acid D to H isotopic ratios were determined via SPME (polyethylene glycol fiber) in conjunction with GCIRMS (Nukol column). Because the concentrations of the indigenous acids were very low for GCIRMS, a bath of dry ice and isopropanol was applied to the outside of the column just below the injector port as a means of combining triplicate SPME loadings into one analysis.

Results and Discussion

At least eleven monocarboxylic acids are present in the extract of the reduced organics poor lithology (11i), including most of the members of the homologous series of linear, saturated monocarboxylic acids from C₁ to C₁₀, two branched, saturated monocarboxylic acids and the aromatic carboxylic acids benzoic acid and its alkyl-substituted derivative 4-methylbenzoic acid (See Table 1 above).

Results and Discussion cont'd

Table 1: Selected GC-MSD Data for the Water Extract of (11i)

Monocarboxylic Acid	Retention Time (min)	Relative Response Factor	Concentration in the Water Extract (ppm)
Formic acid	6.91	1	120
Acetic acid	6.10	2.5	42
Propanoic acid	7.04	5.7	2
Butanoic acid	8.33	11	0.6
Hexanoic acid	13.22	55	0.4
Octanoic acid	20.93	195	0.1
Nonanoic acid	25.65	281	0.4
Decanoic acid	31.09	395	< 0.01

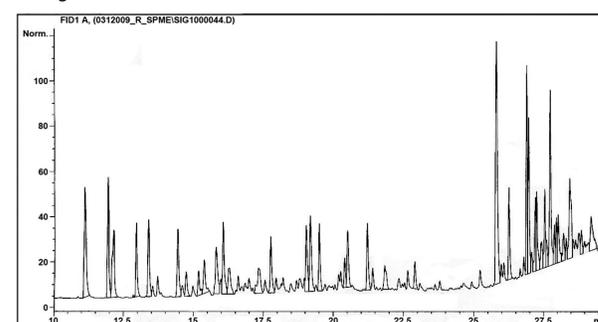
The reduced organics rich lithology (11v) contained all of the acids detected in sample (11i), along with a second branched, saturated monocarboxylic acid and the unsaturated monocarboxylic acid 2-propenoic acid (See Table 2 below).

Table 2: Selected GC-MSD Data for the Water Extract of (11v)

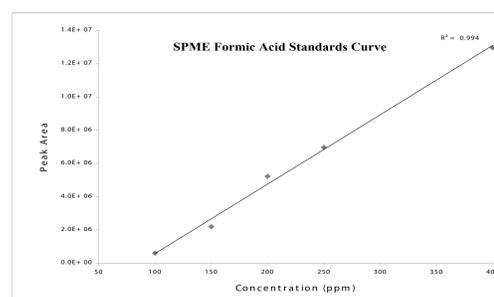
Monocarboxylic Acid	Retention Time (min)	Relative Response Factor	Concentration in the Water Extract (ppm)
Formic acid	6.91	1	200
Acetic acid	6.10	2.5	46
Propanoic acid	7.04	5.7	3.5
Butanoic acid	8.33	11	0.8
Hexanoic acid	13.22	55	0.4
Octanoic acid	20.93	195	0.08
Nonanoic acid	25.65	281	0.2
Decanoic acid	31.09	395	< 0.01

Significantly higher concentrations and a much greater variety of monocarboxylic acids, including many branched isomers, were detected in the water extract for (5B) (Formic Acid conc. = 100 ppm). (See Figure 1 below)

Figure 1 : GC-FID Trace of the Water Extract of (5B)



The identities of all of the straight-chain monocarboxylic acids and benzoic acid were unequivocally established by comparison of their mass spectra/GC retention times to those for authentic samples of the acids. The concentration of the formic acid in each water extract was quantified by referring the peak area to an aqueous formic acid standard curve (vide infra).



Results and Discussion cont'd

We have found unusually high formic acid concentrations in the present study of Tagish Lake, viz. more than 200 ppm for the water extract of (11v) and more than 100 ppm for the water extract of (11i), which are due to a confluence of the following factors: a) The Tagish Lake meteorite has been kept below 0°C since its recovery, which has minimized loss of volatile organics such as formic acid, and b) by analyzing an external standard mixture containing of all of the straight-chain acids present in the meteorite, and by subsequently spiking a subsample of the standard mixture with neat formic acid, we were able to ascertain that the response factor for monocarboxylic acids run on a GCMS (quadrupole) instrument increases asymptotically with increasing chain length and that the response factor for formic acid in this methodology is less than 0.01 of that for the long-chain acid nonanoic acid! Very similar GCMS (quadrupole) response factors were found by a chemical pathology research group in the U.K. during their study of short-chain monocarboxylic acids [14]. Our GCMS results have also revealed that the formic acid to acetic acid ratio is higher for (11v). This implies that the reduced organics-rich lithology contains a more highly oxidized suite of monocarboxylic acids [15]. Lastly, we have recently found that the monocarboxylic acids within Tagish Lake are enriched in deuterium compared to terrestrial organics, with δ D ranging from + 247 to + 697 mil. (See Table 3 below)

Table 3: δ D Values for Some of the Monocarboxylic Acids in the Water Extract of (5B)

Monocarboxylic Acid	δ D Value (mil)
Formic Acid	+247
Acetic acid/Propanoic Acid	+708
Isobutanoic Acid	+493
Butanoic Acid	+562
Isopentanoic Acid	+697

Conclusions

GCMS (quadrupole) analyses of the dichloromethane extracts for (11i) and (11v) revealed much higher concentrations and a greater variety of reduced organics in the extract for (11v). The alkanes in (11v) may very well have been formed by in situ hydrothermal decarboxylation of aliphatic monocarboxylic acids, which are clearly present in high abundance in this lithology [16]. Conversely, the abundant monocarboxylic acids in the reduced organics-poor lithologies (11i) and (5B) may have been generated by either radiolysis of alkane-carbon dioxide mixtures within interstellar grains [17] or the catalytic transformation of alkanes into carboxylic acids on dust grains. Moreover, the δ D results suggest that the acids were generated by the free-radical based mechanism described above, which leads to deuterium enrichment at low temperatures. We will be able to give a better assessment of the origins for the monocarboxylic acids and the antecedent-descendent relationships between the members of the homologous series of straight-chain monocarboxylic acids once the molecule-specific hydrogen isotope studies on the reduced organics in the same Tagish Lake samples are complete.

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