

Quantification of Monocarboxylic Acids From a Spark Discharge Synthesis

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Summary. A suite of sixteen monocarboxylic acids having carbon numbers 2 to 7, formed by the Miller-Urey spark discharge process, were identified and quantified by gas chromatography and mass fragmentography using a deuterium spiking technique. The molar concentration and isomeric distribution of these laboratory synthesized monocarboxylic acids are compared to those previously reported for the Murchison meteorite. They show similar trends, namely, decreasing molar concentration with increasing molecular weight, and, the ratio of normal/branched isomers tend toward smaller with increasing carbon numbers.

Urey) process for making carboxylic acids, with the intention of ascertaining how closely this process resembles the conditions that created the carboxylic acids in the meteorites and, if possible, of gaining some insight about the mechanistic reaction pathway that led to their formation. One means of assessing the pathway is through comparison of the isomeric distribution of compounds obtained under controlled simulated conditions with that found in meteorites. In this paper, the identification and quantification results are reported for the suite of monocarboxylic acids formed by a spark discharge (Miller-Urey type) experiment.

Introduction

Recent identification and quantification of the monocarboxylic acids contained in Murchison meteorite has provided a reliable means for comparing the distribution of straight versus branched chain isomers in the meteorites (Lawless and Yuen 1979, Yuen and Kvenvolden 1973). Knowledge of their isomeric distribution could help elucidate the abiotic process by which these organic compounds were formed. Two prominent processes that are likely to form organic compounds under simulated primordial conditions are the Fischer Tropsch type (FTT) and the Miller-Urey syntheses (Leach et al 1978, Miller 1955, Miller et al. 1976). Either process is capable of converting small molecules (NH₃, H₂O, CH₄, CO, etc.) to large organic molecules including complete suites of monocarboxylic acids. At present, our attention is focussed on the spark discharge (Miller-

Materials and Methods

The reaction apparatus for these experiments consists of a 5 liter flask equipped with two electrodes, one immersed in the solution and the other placed 1.5 cm above the surface of the aqueous solution. The aqueous solution consisted of 100 mL of 0.05 N HCl, adjusted to pH 8 with ammonium hydroxide. After the solution was added to the reaction vessel, the vessel was sealed and immersed halfway into a carbon dioxide-propyl alcohol bath. When its content solidified completely, the vessel was evacuated through a stopcock and then filled with methane and nitrogen. The partial pressure of methane and nitrogen admitted to the vessel were 200 and 100 torr, respectively. This mixture was sparked with a Tesla coil for 24 hours at room temperature, with constant stirring by a magnetic stirrer. The vessel was opened and the contents were filtered. The filtrate was adjusted to pH 11 by addition of solid potassium hydroxide pellets and extracted twice with 25 mL portions of diethyl ether. The ether extract was discarded and the aqueous solution was lyophilized. The resulting residue from lyophilization was transferred to a 16 x 125 mm screw cap culture tube and was acidified to pH 1 with cold concentrated phosphoric acid. One mL of diethyl ether was added to the tube, which was then capped and shaken for intimate mixing.

After the phases separated, a 10 μ l sample of the organic phase, containing the monocarboxylic acids, was analyzed by gas chromatography (Fig. 1). Comparison of this gas chromato-

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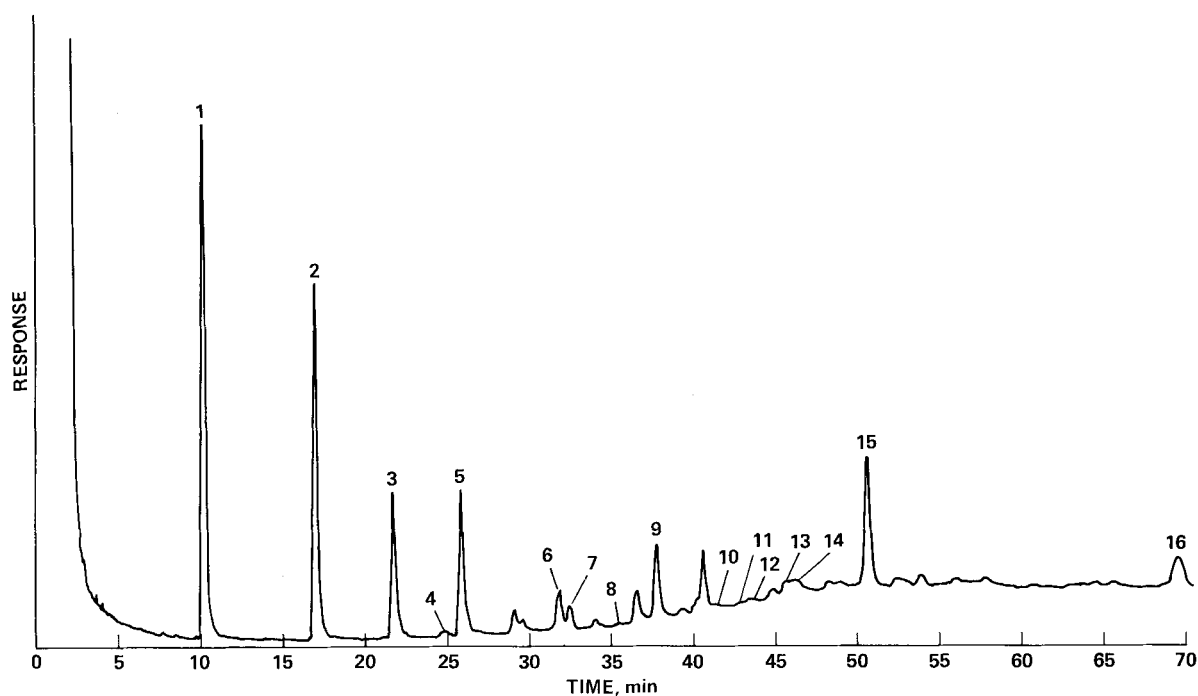


Fig. 1. Gas Chromatogram of the monocarboxylic acids from the spark discharge: (1) ethanoic, (2) propanoic, (3) 2-methylpropanoic, (4) butanoic, (5) 2,2-dimethylpropanoic, (6) 3-methylbutanoic, (7) 2-methylbutanoic, (8) 3,3-dimethylbutanoic, (9) pentanoic, (10) 2,3-dimethylbutanoic, (11) 2-ethylbutanoic, (12) 2-methylpentanoic, (13) 3-methylpentanoic, (14) 4-methylpentanoic, (15) hexanoic^a and (16) heptanoic acids. Chromatographic conditions: Perkin Elmer 3290 (flame ionization) with stainless steel capillary column (46 m x 0.05 cm internal diameter) coated with UCON LB-550X - H₃PO₄. Initial temperature 70^o for 4 min. Temperature program at 1^o min⁻¹ from 70^o-110^oC. Final temperature 110^oC for 120 min.

^a The hexanoic acid peak appears abnormally high, as an impurity present in the controls coeluted under the conditions of this GC run

Table 1. Yields of monocarboxylic acids in micromoles of acids produced per discharge flask containing 54 mmoles of CH₄. Weight of monocarboxylic acids in gram per 10 ml of standard solution

Standard solution acid	Standard solutions g/10 ml		Product Yield	
	Deuterated acid	Non-deuterated acid	Micromoles	Std. dev.
Ethanoic ^a	0.219	0.174	26.9	
Propanoic	0.0821	0.0930	12.3	1.51
2-Methylpropanoic	0.0107	0.0182	0.333	0.152
2,2-Dimethylpropanoic	0.00765	0.00894	0.114	0.0054
Butanoic	0.0289	0.0369	1.85	0.0091
3-Methylbutanoic	0.00914	0.00853	0.142	0.0049
2-Methylbutanoic	0.00873	0.00764	0.284	0.033
3,3-Dimethylbutanoic ^{a,b}	0.00486	0.0162	0.0296	
Pentanoic	0.0147	0.0182	0.535	0.037
2,2-Dimethylbutanoic ^c	0.00898	0.00717		
2,3-Dimethylbutanoic ^b	0.00824	0.0111	0.397	0.274
2-Ethylbutanoic ^b	0.0135	0.00872	0.176	0.165
2-Methylpentanoic ^b	0.0048	0.0148	0.0177	0.0101
3-Methylpentanoic	0.00737	0.00840	0.0614	0.0062
4-Methylpentanoic	0.00725	0.0160	0.0548	0.0069
Hexanoic	0.00877	0.00868	0.0661	0.024
Heptanoic ^b	0.00715	0.00896	0.0190	0.0093

^a Quantitation was based on one pair of ion fragment

^b These values were obtained from region of calibration curve \geq 90% deuterium.

^c Not detected in this experiment

gram with that of a standard solution of deuterated monocarboxylic acids prescribed the quantity of the deuterated solution to be added to the spark discharge extract in order to approximate a 1:1 molar concentration of the monocarboxylic acids from the spark discharge experiment and their deuterated analogs. After adding the deuterated acids and shaking briefly, the ether layer was separated from the aqueous phase. Extraction of the aqueous phase was repeated three times with 1 ml portions of diethyl ether. The combined ether extract was dried with anhydrous sodium sulfate, filtered and concentrated to a small volume (~100 μ L) for analysis by gas chromatography-mass spectrometry (Lawless and Yuen 1979).

The standard solutions of deuterated and non-deuterated monocarboxylic acids which were needed for spiking the spark discharge samples and for calibration purposes, were prepared by adding dichloromethane to each suite of weighed monocarboxylic acids to make a 10 mL solution, as listed in Table 1. Since the relative concentrations of the acids formed in this experiment were not known beforehand, the weight of the individual acids in the standards were selected based on their relative quantities in the meteorite sample.

The calibration curve of the GC-MS quantitation of the spark discharge sample was obtained by analyzing various combinations of the deuterated and non-deuterated standard solutions. In addition to analysis of the standard deuterated and non-deuterated solutions, five combinations of the deuterated and non-deuterated acids solutions were analyzed whose ratios were as follows 1:4, 1:3, 1:1, 3:1, and 4:1 respectively.

The deuterated acids used in this work contain deuterium atoms on the number 2 carbon, except for 2,2-dimethylpropanoic and 2,2-dimethylbutanoic acids, which were deuterium labelled in the methyl group. All these deuterated acids were prepared by D-H exchange using 6 *N* DCl in D₂O, adding D₂O to the corresponding enolate dianion, R-CH=CO₂²⁻, or by C-tri-deuteromethylation of the enolate dianion (Pfeffer and Silbert 1970).

Results

The suite of monocarboxylic acids and their quantities in micromoles are listed in Table 1. There exist in the

gas chromatogram of this experiment a number of unidentified peaks, Fig. 1. Since all the theoretically possible isomeric C₂ through C₆ monocarboxylic acids are included in the standard solution, these unidentified peaks are probably low molecular weight cyclic and/or unsaturated carboxylic acids and those with retention times greater than hexanoic also could be isomeric monocarboxylic acids having more than six carbons. As mentioned in our previous paper (Lawless and Yuen 1979), the peak areas are not necessarily proportional to the concentration of acids found in the sample. Consider, for example, hexanoic acid and its isomer 4-methylpentanoic acid. On the basis of GC peak area hexanoic acid is higher in concentration (Fig. 1), whereas in fact they are almost equal in concentration (see Table 1). The distribution of monocarboxylic acid isomers from the spark discharge experiment were compared to those of the meteorite sample (Table 2). Although a larger number of branched isomers were obtained in the spark discharge, the relative concentrations of the individual branched isomers were considerably smaller than the corresponding normal isomers of equivalent carbon numbers. For example, as shown in Table 1, methyl propanoic acid is about one-fifth the concentration of butanoic acid and the five carbon branched isomers are all on the order of one-quarter to one-half the concentration of the normal isomer. Whereas the concentrations of the individual branched isomers were approximately equal to the concentration of the corresponding normal isomer of equivalent carbon number in the Murchison sample.

Quantitation by this deuterium spiking technique (Summons et al. 1974; Lawless and Yuen 1979) gives the best results when deuterated and non-deuterated compounds are present in equal concentration. For

Table 2. Relative concentrations and R values for the monocarboxylic acids

Monocarboxylic Acids	Spark discharge		Murchison	
	Rel. conc.	R = N/ Σ Br	Rel. conc.	R = N/ Σ Br
Ethanoic	100.0		100.0	
Propanoic	45.7		178.	
2-Methylpropanoic	1.24	5.55	48.	0.76
Butanoic	6.88		36.	
2,2-Dimethylpropanoic	0.42			
3--Methylbutanoic	0.53	0.99	8.7	0.57
2-Methylbutanoic	1.05		12.0	
Pentanoic	1.99		12.0	
3,3-Dimethylbutanoic	0.11			
2,3-Dimethylbutanoic	1.48			
2-Ethylbutanoic	0.65			
2-Methylpentanoic	0.066	0.092		
3-Methylpentanoic	0.23			
4-Methylpentanoic	0.20		6.8	0.86
Hexanoic	0.25		5.8	
Heptanoic	0.071			

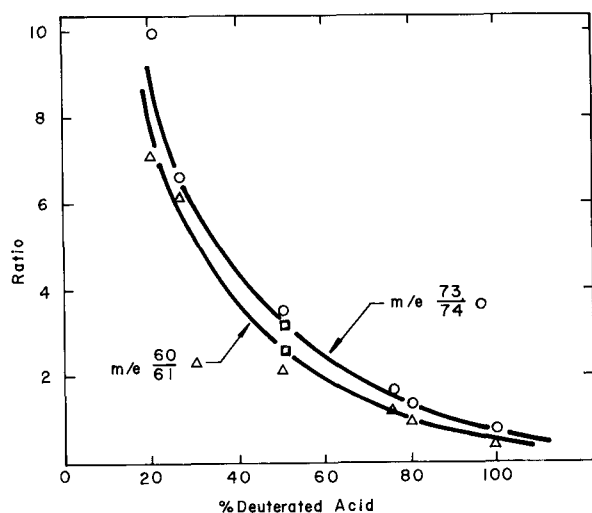


Fig. 2. Quantitation of the butanoic acid present in the spark discharge sample (data points \square) using the calibration curves for the m/e 60/61 and 73/74 ion fragments which were obtained by mass fragmentography of mixture of known concentration of deuterated and non-deuterated butanoic acids

example, quantitation of butanoic acid was achieved by comparing the ratios of peak intensities of the m/e 73/74 and the m/e 60/61 pairs, where m/e 60, 61, 73, and 74 are the mass fragments: $\text{CH}_2=\text{C}(\text{OH})_2$, $\text{CHD}=\text{C}(\text{OH})_2$, $\text{-CH}_2\text{CH}_2\text{CO}_2\text{H}$, and $\text{-CH}_2\text{CHDCO}_2\text{H}$, respectively. Peak ratio 2.3 for the m/e 60/61 fragment pair corresponds to 50.5% deuterium and peak ratio 3.2 for the m/e 73/74 fragment pair corresponds to 50% deuterium, Fig. 2.

The shape of the calibration curve flattens in the region of high deuterated acid concentration. In this relatively flat region, a small difference in ratio of peak intensity results in a large change in deuterated acid content. Those acids with large standard deviation listed in Table 1 have peak intensity ratios corresponding to > 90% deuterated acid content on their calibration curves.

Discussion

By gas chromatography and mass fragmentography of the spark discharge sample, 16 monocarboxylic acids were identified and quantified. With the possible exception of 2,2-dimethylbutanoic acid, all the possible isomers of the saturated monocarboxylic acids up to six carbons were formed by this process. The concentration of these carboxylic acids decreased as their carbon number increased, Table 2. A similar trend was observed in the Murchison samples, but the decrease in concentration with increasing carbon number is more precipitous in the spark discharge sample.

Leach et al. 1978 reported the formation of 6 to 18 carbon monocarboxylic acids by the Fischer-Tropsch type (FTT) process and observed that this process favored formation of the normal isomer in preference

to the branched chain isomers. This preference was expressed as $R = N/\Sigma Br$, where R is the ratio, N is the molar concentration of normal isomer and ΣBr is the sum of the molar concentrations of the branched isomers having the same molecular formula. R values greater than unity would indicate that the normal isomer is in preponderance, whereas R values less than unity indicate that the sum of the molar concentration of branched chain isomers exceeded the molar concentration of the normal isomer. R values reported the monocarboxylic acids formed by the Fischer-Tropsch process varied between 1.7 to 5.0.

The R values of the monocarboxylic acids from the spark discharge and Murchison meteorite samples are listed on Table 2. Since different numbers of branched isomers are under consideration, comparison of the R values in this table should be viewed only in a qualitative manner. R values for the four carbon isomers are quite different, 5.6 for the spark discharge and only 0.76 for the Murchison sample. The R values for the five and six carbon isomers show a similar trend, with values for the C5 isomers of 1.0 for the spark discharge and 0.57 for the Murchison sample, and values for the C6 isomers of 0.092 for the spark discharge and 0.86 for the Murchison sample. Although the R values for the spark discharge and the Murchison samples do not agree in all details, they show sufficient similarity to suggest that the spark discharge process is capable of producing the variety and quantities of isomers found in the Murchison meteorite. Unfortunately, the isomeric distribution data for the C2-C6 monocarboxylic acids from the FTT synthesis are not available for direct comparison with those found in Murchison and the spark discharge process. Since R values for the FTT synthesis of the C8-C18 acids clearly favors formation of the normal acids, it would not be surprising to find that the same preference exist for the C4-C6 acids. These R values suggest that the spark discharge process is a better model system for the abiotic process that formed the monocarboxylic acids found in the Murchison meteorite than is the Fischer-Tropsch reaction.

The monocarboxylic acids formed in the spark discharge process do show trends similar to the acids found in the Murchison samples, namely — decreasing molar concentration with increasing molecular weight, and the ratio of normal/branched isomers (R) tend toward smaller values with increasing carbon numbers. While this latter trend is consistent with the prediction based on the rapid increase in number of branched isomers possible with each added carbon, there seems to be a slight preference for forming the normal isomer. This preference is noted for the 4, 5 and 6 carbon monocarboxylic acids, but for one exception the amount of the normal isomer is equal to, if not greater than any individual branched isomer. Projecting on the basis of 4, 5 and 6 carbon, this preference should prevail with the higher homologous also. This finding is not in accord

with previous work that reported the formation of predominantly the normal isomers of C4 and C5 monocarboxylic acids and branched isomers only for those acids with 6 to 12 carbons (Allen and Ponnampereuma 1967; Miller and Orgel 1974). In fact, two normal acids having more than five carbons are included in this paper.

In summary, although the spark discharge experiment conducted under the conditions described herein does not adequately account for the monocarboxylic acid distribution in the Murchison meteorite, it does show sufficient similarity to justify further studies of the spark discharge process. The data presented do support the contention that the amino acids and monocarboxylic acids may have been formed from common precursors, as evidenced by similar distribution with respect to molecular weight. The data also support the hypothesis that complex organic molecules, such as monocarboxylic acids, were built up by synthesis from simple precursors. Because of the variation of product distribution with specific reaction conditions in the Fischer-Tropsch type, spark discharge, and by other synthetic pathways (Anders et al. 1973; Eck et al. 1966), it is possible that the reaction mechanism of formation of organic compounds in meteorites cannot be conclusively determined by studies of structure and isomeric distribution alone. However, these studies, when correlated with studies of isotopic composition and mineralogy have the potential to provide meaningful answers. It has been suggested that the types of reactions described here may have also played a role in the origin of life-first, by converting carbon to a sufficiently non-volatile form to allow its accretion by the inner planets,

and secondly, by synthesizing organic compounds on the primitive planets, whenever the proper precursor molecules and inorganic catalysts were brought together under the proper reaction conditions (Anders et al. 1973; Kenyon and Sternman (1969)).

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