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Formation of Carboxylic Acids from Elemental Carbon and Water by Arc-Discharge Experiments

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Synopsis. Mono- and dicarboxylic acids formed from elemental carbon and water by arc-discharge experiments show a systematic decreases along with an increase in the carbon number. The formation of carbon chains of these acids likely proceeded by a progressive additon of one carbon species; this process is discussed in relation to those acids found in carbonaceous chondrites.

Since the successful work by Miller,[1)] numerous experimental studies have been carried out concerning the formation of biologically interesting organic compounds under simulated prebiotic conditions on the primitive Earth and elsewhere in the solar system. Among these studies, two types of organic syntheses have been employed rather frequently: One is a Miller–Urey type synthesis in which a gas mixture consisting some of CH_4, CO, NH_3, N_2, H_2O, and H_2 is exposed to an electric discharge inducing chemical reactions;[2)] the other is a Fischer–Tropsch type synthesis at elevated temperature with a gas mixture of common CO and H_2 (occasionally includes NH_3 or N_2) in the presence of a heterogeneous catalyst for hydrogenation.[3)] These studies are based on the idea that primordial organic compounds were formed from the gaseous constituents in the primitive Earth atmosphere and in the early solar nebula.

Meanwhile, another type of abiotic syntheses has been performed by the reaction of atomic carbon generated from graphite electrodes. These reported studies are only several and include the formation of amino acids in the presence of ammonia[4)] and carbohydrates in the presence of water.[5)] Along this line of syntheses, we examined the formation of mono- and dicarboxylic acids in experiments using graphite and water as the only sources of carbon, hydrogen, and oxygen. The two types of carboxylic acids formed show unique molecular distribution patterns that can be used as a criterion concerning the primary products and postulate a reaction that is probably related to the prebiotic formation of these acids in the early solar system.

Apparatus and Procedures

The syntheses of carboxylic acids were performed using the apparatus shown in Fig. 1. Two graphite rods were set vertically through the top and bottom necks of a 330 cm^3 separable flask. The rods were Hitachi Spectroscopic Graphite Electrodes, Sp. Grade, Hitachi Kasei Co. The upper rod was 5 mm in diameter and 150 mm long, and the lower one was 8 mm in diameter and 305 mm long. One hundred cm^3 of water was placed in the flask and argon gas was flown in from one neck and out from another at a rate of 50 $cm^3\ min^{-1}$ throughout the discharge experiment. An intermittent arc between the two graphite rods was generated by a power source (Small Discharge Instrument, Sparky W-700, Motofuji Co.) set at 7 A and 100 V. The driving unit was used to gradually lower the upper rod as its tip vaporized during the continuation of the discharge. The flask was kept at less than 30 °C by circulating ice-cooled water.

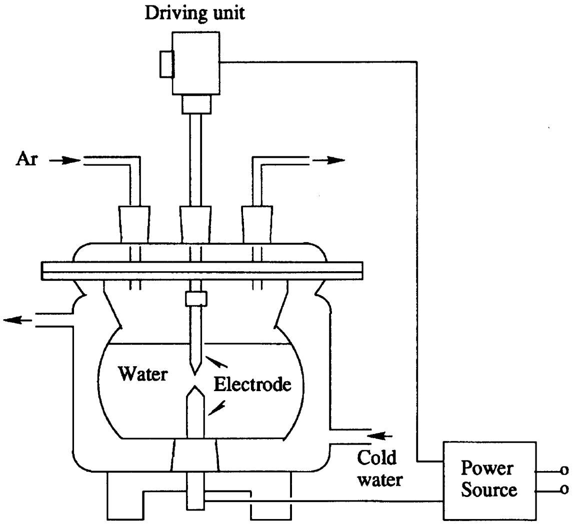

Fig. 1. Schematic drawing of the apparatus used for the arc-discharge experiment.

After a 60 min discharge, the water solution was recovered. An aliquot of the solution was passed through a 0.45 μm Millipore filter and brought to pH 12 by adding 2 $mol\,dm^{-3}$ KOH solution. This solution was reduced to about 1 cm^3 and adjusted to pH 2 by a 2 $mol\,dm^{-3}$ HCl solution. The acidified solution was extracted by 1 cm^3 dichloromethane five times. The combined dichloromethane was carefully concentrated by a Kuderna–Danish type concentrator. The volume of the concentrated solution was adjusted and examined for monocarboxylic acids by a gas chromatograph (GC) coupled to a mass spectrometer (MS) (Simadzu GCMS QP-1000A).

Another acidified solution after the dichloromethane extraction (separately prepared) was evaporated to dryness and treated by 1 cm^3 of 15 % wt boron trifluoride (BF_3) in methanol at 85 °C for 30 min. One cm^3 water was added to the methanol solution, from which dimethyl esters of dicarboxylic acids were extracted by 1 cm^3 benzene five times. The combined benzene solution was concentrated by the concentrator and examined by the GC/MS method.

The GC was operated with a FFAP FS-WCOT capillary column (50 m×0.25 mm i.d.) from 90 to 180 °C at a rate

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of 2 °C min^{-1}. The MS was scanned every 1.5 s over m/z 32 to 300 in the electron-impact mode at 70 eV and when necessary, in the chemical-ionization mode at 200 eV with isobutane as reacting gas. The obtained data were stored in a GC/MS computer with a library search system containing 39750 compounds of the National Bureau of Standards, U.S.A.

Identification of the compounds was made by the GC/MS method using standard compounds and the library. Quantification was performed from peak areas on gas chromatograms in comparison with those of the standards by using another GC (Shimadzu GC 12A) equipped with the same GC column and a FID detector.

All glassware was heated at 500 °C at least for 3 h prior to use in order to eliminate any possible organic contaminants. The water was distilled, deionized, and redistilled. Organic solvents were distilled prior to use. The 15% BF_3 in methanol was prepared by bubbling BF_3 gas into distilled methanol.

Results and Discussion

The monocarboxylic acids which were identified and quantified were from acetic acid to hexanoic acid and are listed in Table 1. Since 2- and 3-methylbutanoic acids elute at the same time on the GC column and their mass spectra are very similar, no precise determination concerning the presence of either or both compounds can be made. The arc discharge consumed approximately 200 mg of the graphite electrodes. Therefore, the yield of acetic acid, for example, was roughly 0.0023% on the basis of carbon from the graphite.

Among these compounds, seven (or possible eight) were saturated acids and two were unsaturated ones. The normal saturated acids were more abundant than the branched ones among the C_4 and possibly C_5 acids. The detection of only hexanoic acid among the C_6 acids is indicative of normal structure preference. Although other C_6 acids were probably formed, the amount of each isomer was too small to be detected, because of the formation of a maximum of eight isomers against four for the C_5 acids. The amounts of the normal acids decreased with an increase in the carbon number of the molecules.

The formations of carbonic and formic acids were highly likely, although they were not found by the present method. However, it should be mentioned here that the two acids were detected in amount much more than acetic acid in a separate arc discharge experiment with a modified setting of the graphite electrodes in water and a detection method using an ion chromatograph (Dionex 2000i, Dionex Co.) which enabled us to examine the product solution directly without any concentration processes or chemical treatment.

A total of seven compounds were identified for dicarboxylic acids formed by the arc-discharge experiment. Their identifications and amounts are listed in Table 1. These seven include four normal acids and one branched acid as well as two unsaturated acids. The yield of the most abundant oxalic acid was about 0.0075% on the basis of carbon from the graphite. The yields of the normal acids decreased with an increase in the carbon number of the molecules. Only the smallest compounds were found for the branched structure (2-methylsuccinic acid, *i*-C_5) and the unsaturated acids (fumaric and maleic acids, *trans*- and *cis*-$C_{4:1}$, respectively).

Since we did not analyze compounds other than carboxylic acids, we may only speculate the mechanisms involved in the formation reaction of the acids. A temperature of roughly 6000 K has been reported for the arc stream[6)] and a rather lower temperature of about 3800 K at the electrode surface due to the sublimation of graphite.[7)] Under these vigorous conditions, water molecules dissociate to H atoms and OH radicals in addition to the generation of carbon atoms from the graphite rods. Therefore, in our experiments H atoms were probably used to from C–H bonds, which contributed to the formation of carbon chains, while OH radicals reacted with the carbon atoms to form alcohols. The OH radicals were sufficiently abundant to oxidize the alcohols to aldehydes and, further, to carboxylic acids.

A common characteristic feature of the mono- and dicarboxylic acids formed was a decrease in the amount with an increase in the carbon number of the normal structures. This result is shown in Fig. 2, where semilogarithmic linear relations exist between the amounts of molecules and their carbon numbers. These linear relations suggest that the detected carboxylic acids were primary products and not altered secondary ones in the discharge experiment. In additon, these relations postulate a synthetic reaction in which larger molecules are formed from smaller ones in the homologues by

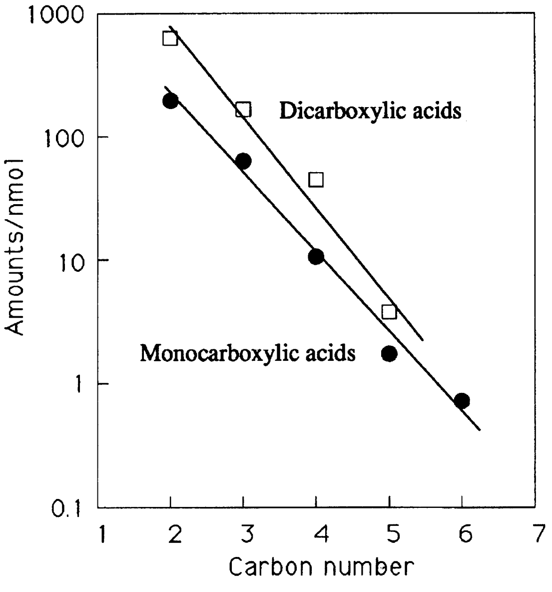

Fig. 2. Amounts versus carbon number of mono- and dicarboxylic acids formed from graphite and water by the arc-discharge experiment.

Table 1. Mono- and Dicarboxylic Acids Formed from Graphite and Water in the Arc-Discharge Experiment (amount in nmol)

Monocarboxylic acid[a]	Amounts	Dicarboxylic acids[a]	Amounts
Acetic acid	196	Oxalic acid	624
Propionic acid	63.3	Malonic acid	166
2-Methylpropionic acid	5.4	Fumaric acid	6.7
Butanoic acid	10.6	2-Methylsuccinic acid	4.9
Propenoic acid	5.5	Succinic acid	44.7
2-Methylbutanoic acid and/or 3-Methylbutanoic acid	2.4	Maleic acid	15.0
		Glutaric acid	3.8
Pentanoic acid	1.8		
2-Butenoic acid	1.5		
Hexanoic acid	0.7		

a) These compounds are listed in order of retention times of the GC columns.

the addition of one carbon species. A similar reaction has been proposed for the formation of monocarboxylic acids (C_2—C_5) found in the Murchison carbonaceous chondrite.[8] The carbon isotope composition of these acids systematically decreases in $^{13}C/^{12}C$ with increasing carbon number in the straight-chain homologue, suggesting carbon-chain formation by a progressive addition of carbon atoms in a kinetically controlled process. In that synthesis CO was likely to be the initial carbon source material against the graphite in ours.

The straight lines in Fig. 2 can be written using a least-squares fit as

$$\log C_M = -0.61n + 3.5$$

and

$$\log C_D = -0.72n + 4.3$$

where C_M and C_D are the amounts (in nmol) of mono- and dicarboxylic acids, respectively, and n is the carbon number. The coefficients of correlations for the lines are 99.4 and 98.6% for the mono- and dicarboxylic acids, respectively. The slopes (−0.61 and −0.72) indicate that the amounts decrease to 22 and 19%, respectively, by each addition of one carbon species. A similar straight line with a slope of ca. −0.7 was reported in log concentration versus carbon number for the straight-chain amino acids (C_2—C_7) recovered from the Murchison chondrite.[9] Therefore, the carbon chains of these amino acids were likewise formed by the addition of one carbon species.

In conclusion, the current arc-discharge experiment produced mono- and dicarboxylic acids from elemental carbon (graphite) and water, although their yields were very small. These acids present a common characteristic feature in amount versus the carbon number. This feature indicates that the acids are primary products, and provide useful information concerning a synthetic reaction which could be similar to that which takes place in the prebiotic formation of carboxylic acids as well as amino acids in carbonaceous chondrites in the early solar system.

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