Sulfur and Hydrogen Isotope Anomalies in Meteorite Sulfonic Acids

George W. Cooper,* Mark H. Thiemens, Teresa L. Jackson, Sherwood Chang

Intramolecular carbon, hydrogen, and sulfur isotope ratios were measured on a homologous series of organic sulfonic acids discovered in the Murchison meteorite. Mass-independent sulfur isotope fractionations were observed along with high deuterium/hydrogen ratios. The deuterium enrichments indicate formation of the hydrocarbon portion of these compounds in a low-temperature environment that is consistent with that of interstellar clouds. Sulfur-33 enrichments observed in methanesulfonic acid could have resulted from gas-phase ultraviolet irradiation of a precursor, carbon disulfide. The source of the sulfonic acid precursors may have been the reactive interstellar molecule carbon monosulfide.

Previous isotopic measurements of organic compounds from the Murchison meteorite, a carbonaceous chondrite, have shown that water-soluble polar organic compounds generally have high 2H/H (D/H), 13C/12C, and 34S/32S, and 15N/14N ratios relative to Earth and solar system ratios (1). The origins of such isotopic enrichments have been attributed to precursors formed in low-temperature (≈10 to 200 K) interstellar clouds by grain surface and gas-phase ion-molecule reactions (2). After incorporation into the proto-solar system and meteorite parent bodies at about 4.5 billion years ago, the interstellar precursors reacted during a period of aqueous alteration to form some of the observed meteoritic compounds (3).

The finding of homologous series of organic alkyl sulfonic acids (Scheme 1A) and phosphonic acids (Scheme 1B) (R = CnH2n+1) in Murchison is of interest because, in meteorites, the sulfonic acids are the first well-characterized series of organic S compounds, and the phosphonic acids are the only identified organic P compounds (4). In addition to D/H and 13C/12C measurements, our objective was to determine if the sulfonic acids had unusual S isotope ratios. Such anomalies in the sulfonic acids, along with unusual ratios of H and C isotopes in both classes of compounds, may demonstrate that at least some meteorite organic compounds containing S and P are traceable to origins in interstellar clouds or the proto-solar nebula.

In systems involving only two stable isotopes, such as C, H, and N, it is difficult to discriminate between ordinary mass-dependent isotopic fractionation (for example, evaporation or other kinetic isotope effects) and mass-independent processes such as nucleosynthesis or symmetry-dependent chemical mechanisms. Studying an element with four stable isotopes, such as S, removes this limitation by allowing one to observe graphically the deviation of an isotope from mass-dependent behavior (5). Recently, some bulk ureilite meteorites have been shown to have small 33S excesses (0.1 per mil) (7), and excess 33S (-0.16 per mil) was found in an oldhamite (CaS) separate from the Norton County enstatite meteorite (8).

We examined the methyl (MSA), ethyl (ESA), isopropyl (iPSA), and n-propyl (nPSA) sulfonic acids. The extraction from Murchison and the separation of sulfonic acids (sulfonics) and phosphonic acids (phosphonics) from other fractions of Murchison compounds were done as described in (9). We achieved baseline chromatographic separation of individual sulfonics (10). The phosphonics are present in very small amounts in Murchison (4); therefore, only bulk isotopic measurements were attempted (Table 1).

In Murchison MSA, 33S, 34S, and 35S (Table 1) are enriched relative to their abundances in various organic and inorganic phases from several meteorites (6–8, 11). The corresponding 8S values of the other sulfonic acids fell within a range previously observed for organic phases in Murchison and other carbonaceous chondrites (11). The S isotopic distribution of MSA also shows an anomalous mass-independent enrichment (5) in 33S of 3.2 ± 1.9 per mil. The 3Δ value of iPSA is zero within measurement uncertainty; however, the 3Δ values of ESA and nPSA, although small, are anomalous (Table 1). Present measurements of 35S have greater uncertainty than those of other S isotopes (Table 1) because of its low natural abundance (0.02%) coupled with the small (micromolar) sample sizes. Corresponding 3Δ values are of course also less certain. In MSA, the largest sample, 836S, is about the value expected for a mass-dependent process, 836S = 2836S (5).

The 813C values of the sulfonics decrease with increasing carbon number, as observed with homologous series of carboxylic acids and hydrocarbons from Murchison (12). In relation to the known 813C values of Murchison organic compounds, the 813C values of the sulfonic acids span the range from those of the amino acids to those of the carboxylic acids (6–40 to 51). As with the results obtained on Murchison amino acids (13), the D/H ratios of the sulfonics substantially exceed terrestrial ratios, indicating formation of the C–H bonds in a region that allows such D enrichment, that is, a low-temperature environment like that in interstellar clouds (2). In comparison with the D/H ratios of other Murchison organic compounds, the sulfonics fall in the range of the polar hydrocarbons and insoluble C (6D – 500 to 1000) (1). Because the phosphonic acids are present in small amounts, their isotope ratios are not corrected and are minimum values. Their D/H ratios are also above terrestrial ratios (Table 1).

Any proposed mechanism for sulfonic acid formation must account for the following observations: (i) the magnitudes of the 8C, 8S, and 3Δ values of MSA and the lower corresponding values of the other sulfonics; (ii) the similarity in structure coupled with a decline in abundance of the sulfonic acids with increasing carbon number (4), as with other homologous series of meteoritic organic compounds (1); and (iii) the similar D/H ratios among homologs. The second observation would seem to indicate formation of the sulfonics by the same or closely related processes. The relatively constant D/H ratios of the sulfonics could imply that unsaturated precursors (C2S) to the sulfonics were formed first, followed by hydrogenation and D enrichment in a pool of nearly uniform H. The D/H values of the sulfonic acids as a group are nearly identical to those of Murchison polar hydrocarbons and insoluble carbonate material (1), which raises the possibility that C–H bonds of the precursors to the three groups were formed in the same pool of H.
The isotope effects may derive from molecules such as CS₂ (14), CO₂, and O₃ (15). CS₂ forms several molecules and in interstellar space (2). In the laboratory, mass-independent sample of Murchison. The matching bulk sample was lost. Procedural standards, MSA: 1, 1.4, and 7 F.mol. H

The 8D values are corrected for blank and exchangeable hydrogen. In contrast to C and S, less than quantitative yields of H were obtained for MSA and nPSA. However, measurements of a standard (NBS-22) with the same vacuum and combustion procedure indicated no D/H or ac/ac fractionation, and procedural standards consisting of different amounts of MSA showed close agreement, ±4, of 8D values (above). This value is obtained after correcting for exchangeable hydrogen only. From a different sample of Murchison. The matching bulk sample was lost. Procedural standards, MSA: 1 and 7 ac/ac.

Table 1. Results of intramolecular measurements of stable isotopes of S, C, and H, from Murchison sulfonic acids. Uncorrected 813C values (in per mil) from a previous experiment with comparable amounts of sample are as follows: MSA, 25.4; ESA, 4.8; nPSA, 1.8; pPSA, ~11.2. These are left uncorrected because of uncertainties in blank CO₂ amounts. The corresponding 83S value of MSA was 1.24 per mil (25). In a preliminary experiment, 813C values were also lower (30); however, because of refined procedures, the present sulfonics are purer isolates. The errors in measurement of samples are those of the corresponding procedural standard. Although the amount of sulfur in the procedural blank was so small that the resulting silver sulfide [see procedures in (6)] could not be weighed, a small amount was seen (as SO₂) on the ion chromatogram, a maximum of ~0.3 μmol. 813C values are blank corrected. The standards used for 813C and 8D measurements were Pee Dee belemnite and standard mean ocean water, respectively. All isotope values are given in per mil.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Amount (μmol)</th>
<th>813C</th>
<th>8D</th>
<th>83S</th>
<th>84S</th>
<th>833S</th>
<th>834S</th>
<th>8332</th>
</tr>
</thead>
<tbody>
<tr>
<td>R(in R-SO₃)</td>
<td>3.8</td>
<td>29.8</td>
<td>483</td>
<td>7.63</td>
<td>11.27</td>
<td>22.5</td>
<td>2.00</td>
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<tr>
<td>CH₃ (MSA)</td>
<td>1.7</td>
<td>9.1</td>
<td>767</td>
<td>0.33</td>
<td>1.13</td>
<td>0.8</td>
<td>-0.24</td>
<td></td>
</tr>
<tr>
<td>C₂H₅CH₂CH₂CH₃ (nPSA)</td>
<td>0.9</td>
<td>-0.4</td>
<td>536</td>
<td>0.20</td>
<td>1.20</td>
<td>2.1</td>
<td>-0.40</td>
<td></td>
</tr>
<tr>
<td>CH₃CH₂CH₅ (PESA)</td>
<td>0.7</td>
<td>-0.9</td>
<td>652</td>
<td>0.32</td>
<td>0.68</td>
<td>2.9</td>
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<tr>
<td>Bulk R-SO₃ tà</td>
<td>6</td>
<td>600</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Phosphonic (uncorrected)</td>
<td>-20</td>
<td></td>
<td>219</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Blank</td>
<td>-21.6</td>
<td>-55</td>
<td></td>
<td></td>
<td></td>
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<td>Standard MSA</td>
<td>-39.1</td>
<td>-100</td>
<td>0.45</td>
<td>0.80</td>
<td>2.7</td>
<td>0.03</td>
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<tr>
<td>Standard 1 §</td>
<td>-42.2 ± 0.3</td>
<td>-107 ± 4</td>
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<tr>
<td>Standard 2 §</td>
<td>-29.8</td>
<td>-122</td>
<td>-0.25 ± 0.05</td>
<td>-0.51 ± 0.1</td>
<td>-1.0 ± 1.0</td>
<td>0.00 ± 0.05</td>
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<tr>
<td>NBS-22 standard ¶</td>
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**REFERENCES AND NOTES**

5. Also see (13). The stable isotopes of S have masses of 32 (95.02%), 33 (0.75%), 34 (4.21%), and 36 (0.02%) atomic mass units (amu). The deviation of the ratio of S isotopes in a sample from the standard (S in the Canyon Diablo iron meteorite) is given in parts per thousand or per mil, which is defined as 8S = [(8S/32S)sample/(8S/32S)standard] − 1 × 1000, where X = 33, 34, or 36. Plotted on a three-isotope graph, normal mass-dependent fractionations should lie on the line 83S = 0.5 84S, because the difference between 83S and 84S is 1 amu and the difference between 84S and 86S is 2 amu, which gives 0.5 as the slope. Similarly, 832S = 1.97 843S. Therefore, any mass-independent isotopic anomaly in 83S and 84S is given by (in per mil) 83S = 83S − 0.5 84S and 84S = 84S − 1.97 83S, respectively. All known terrestrial S lies on normal mass-dependent fractionation lines. The calculation of 8 values for C and S is similar to that of S, that is, 8H = [(8H/1H)sample/(8H/1H)standard] − 1 × 1000, where H and L refer to the heavy and light isotopes, respectively, of each element.

10. The fraction containing the sulfonics and phosphonics (6) was then injected into a Dionex (Sunnyvale, CA) ion chromatograph (IC) equipped with two 9 mm × 250 mm AS-4A columns and eluted with a carbonate buffer, 1.8 mM Na₂CO₃ + 1.7 mM NaHCO₃ (4 mM/L), to collect sulfonics and phosphonics as separate groups. At this step, nPSA separates sufficiently from the other sulfonics for collection.
Discrete Intensity Jumps and Intramolecular Electronic Energy Transfer in the Spectroscopy of Single Conjugated Polymer Molecules

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Single-molecule fluorescence spectroscopy of a multichromophoric conjugated polymer (molecular weight ~20,000) revealed surprising single-step photobleaching kinetics and abrupt jumps in fluorescence intensity. These jumps were shown not to result from spectral diffusion and were attributed to fluctuations in the quantum yield of emission for the molecules. The data indicate efficient intramolecular electronic energy transfer along the polymer chain to a localized fluorescence-quenching polymer defect. The defects are created by reversible photochemistry of the polymer. These findings have implications for the use of conjugated polymers in light-emitting diode displays and sensors.

Recent developments in fluorescence microscopy have allowed for the detection, imaging, and spectroscopy of single molecules at room temperature (1-12). As a consequence, single-molecule spectroscopy (SMS) has moved from studies at cryogenic temperatures (13) to a broader range of environmental conditions. In many cases, direct information about the molecular distribution of physical quantities, rather than just the ensemble-averaged values obtained by bulk measurements, can now be obtained. Most room-temperature SMS studies have involved aromatic dye molecules that correspond to a single chromophore in a fluctuating environment and have revealed direct information on chemical and spectroscopic heterogeneity of single molecules (4, 14), as well as on the dynamics of these inhomogeneities (10, 15).

Here, we used SMS to study molecules that each comprise many similar chromophores, such as conjugated fluorescent polymers. Intramolecular migration of energy among these chromophores and the ultimate impact of the energy migration on photochemistry is of intense fundamental and practical interest. Conjugated polymers such as poly(p-phenylene vinylene) (PPV) and poly(p-phenylenevinylene) (PPVY) have shown great promise for light-emitting device applications (16, 17). We studied a derivatized PPV-PPVY copolymer compound with a molecular weight of ~20,000 (Fig. 1A).

Spectroscopic studies on bulk polymer materials suggest that conjugated polymer emission is often dominated by energy migration to local minima in their optical band structure (18). For example, anthracene-derivatized poly(p-phenylene-ethynylene) in solution have been shown to selectively emit from states associated with the anthracene end groups (19). Although excitation diffusion along the chains in conjugated polymers is efficient, the actual optical excitation (exciton) may be localized and may have a coherence length of only a few monomer units (20). Thus, spectroscopic evidence of conjugated polymers suggests that their broad absorption spectra are the result of overlapping absorption bands from different segments along the polymer chain, and that their emission is strongly affected by energy migrations, often to sites remote from the absorption (18). This hypothesis can be