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 $^{2}H/^{1}H$ (D/H), $^{13}C/^{12}C$, and $^{15}N/^{14}N$ ratios relative to terrestrial samples (1). The origins of such isotopic enrichments have been attributed to precursors in molecules 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 meteorite compounds (3).

The finding of homologous series of organic alkyl sulfonic acids (Scheme 1A) and phosphonic acids (Scheme 1B) ($R = \text{C}_n\text{H}_{2n+1}$) 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 $^{13}C/^{12}C$ measurements, our objective was to determine if 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-independent 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, 6). Recently, some bulk ureilite meteorites have been shown to have small $^{32}S$ excesses (~0.1 per mil) (7), and excess $^{33}S$ (~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, $^{33}S$, $^{34}S$, and $^{35}S$ (Table 1) are enriched relative to their abundances in various organic and inorganic phases from several meteorites (6-8, 11). The corresponding $^{18}O$ values of the other sulfonics fall 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 $^{33}S$, $^{34}S$, and $^{35}S$ with $^{32}S$ of $^{3}\Delta = 2.0$ per mil. The $^{3}\Delta$ value of iPSA is zero within measurement uncertainty; however, the $^{3}\Delta$ values of ESA and nPSA, although small, are anomalous (Table 1). Present measurements of $^{33}S$ 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 $^{3}\Delta$ values of ESA and nPSA, although small, are anomalous (Table 1).

*To whom correspondence should be addressed.

Scheme 1

G. W. Cooper, SETI Institute and NASA Ames Research Center, MS 239-4, Moffett Field, CA 94035, USA. S. Chang, NASA Ames Research Center, MS 239-4, Moffett Field, CA 94035, USA. M. H. Thiemens and T. L. Jackson, Department of Chemistry and Biochemistry, University of California, San Diego, La Jolla, CA 92093-0356, USA.

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The difference in S isotope composition between MSA and the other sulfinics likely arises from the differential fractionation factors associated with the formation of the individual molecules. A potential source of the 33S enrichment in MSA (33Δ = 2.0 per mil) could be gas-phase ultraviolet (UV) irradiation of a precursor molecule such as CS3. In the laboratory, mass-independent isotope effects have been produced by the gas-phase UV irradiation of symmetric molecules such as CS3 (14), CO2, and O2 (15). The isotope effects may derive from molecular symmetry factors (16). In the irradiation (313-nm wavelength) of CS3 (14), a 33S excess of 5.3 per mil was observed in the resulting solid phase, which was characterized as (CS3)3. In that experiment, a large 33S deficit was also observed, which is not the case for Murchison MSA. Recent experiments (17), however, have shown the process to be wavelength dependent, and the sign of the fractionations may be reversed. At present, it may only be concluded that a process capable of producing a 33S excess exists in an astrophysical environment.

At the low temperatures of interstellar space, chemical reactions of the molecule CS are capable of producing compounds that could serve as sulfonic acid precursors and have mass-independent isotope anomalies resulting from gas-phase UV irradiation. CS is reactive and relatively abundant in interstellar space (2). In the laboratory, CS forms several molecules and an insoluble solid phase on surfaces when it is condensed at low temperatures (18, 19). Molecular formation in the solid phase has been reported at temperatures as low as 33 K (20). The C/S ratio of the solid usually ranges from 1/1 to 5/1 (18). The requirements of a surface and low temperatures for CS polymerization are met by interstellar grains. In addition, CS will self-polymerize or is stable in the presence of some potentially interfering interstellar compounds. For example, CS is stable in the presence of solid methanol (21) and ammonia (22) and polymerizes in the presence of liquid methanol (21). In the photolysis of CS2 (which produces CS), formation of a solid phase was not prevented by the addition of excess hydrogen and other molecules (23).

The CS reaction products or interstellar molecules of relevance to the present study are CS3 (SCS), CS4 (CCS), CS5 (SCCS), CS6 (CCCSS), and CS7 (CCCSS) (24). These compounds are potential precursors to the observed meteoritic sulfonic acids of the same carbon number. A high-resolution mass spectrometry study of organic matter in the Murray carbonaceous meteorite identified species of elemental compositions CS2, CS3, CS4, CS5, and CS6, in addition to many others (25). CS3 is commonly seen in carbonaceous meteorites (25, 26). In addition, in the present study, the unsaturated analog of ESA, vinyl sulfonic acid (H2C=CH(SO3)2), was identified in an extract of a Murchison sample. These observations reinforce the possibility that the sulfinic and perhaps other interstellar carbon-chain compounds arose from unsaturated precursors, resulting from CS chemistry. Compounds of the type CS2S, if definitely identified in meteores, comets, or interstellar clouds, may be more indicative of a reactive S-rich starting material like CS.
Discrete Intensity Jumps and Intramolecular Electronic Energy Transfer in the Spectroscopy of Single Conjugated Polymer Molecules

David A. Vanden Bout, Wal-Tak Yip, Dehong Hu, Dian-Kui Fu, Timothy M. Swager, Paul F. Barbara*

Single-molecule fluorescence spectroscopy of a multichromophoric conjugated polymer (molecular weight ~20,000) revealed surprising single-step photo-blinking 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) (PPV) have shown great promise for light-emitting device applications (16, 17). We studied a derivatized PPV-PPV 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 migration, often to sites remote from the absorption (18). This hypothesis can be