

Atmospheric Chemistry of Micrometeoritic Organic Compounds

M. E. Kress • C. L. Belle • G. D. Cody • A. R. Pevyhouse • L. T. Iraci

Abstract Micrometeorites ~100 μm in diameter deliver most of the Earth's annual accumulation of extraterrestrial material. These small particles are so strongly heated upon atmospheric entry that most of their volatile content is vaporized. Here we present preliminary results from two sets of experiments to investigate the fate of the organic fraction of micrometeorites. In the first set of experiments, 300 μm particles of a CM carbonaceous chondrite were subject to flash pyrolysis, simulating atmospheric entry. In addition to CO and CO₂, many organic compounds were released, including functionalized benzenes, hydrocarbons, and small polycyclic aromatic hydrocarbons. In the second set of experiments, we subjected two of these compounds to conditions that simulate the heterogeneous chemistry of Earth's upper atmosphere. We find evidence that meteor-derived compounds can follow reaction pathways leading to the formation of more complex organic compounds.

Keywords micrometeorite • organic chemistry • atmosphere

1 Introduction

Micrometeorites ~100 μm in diameter carry most of the extraterrestrial material striking the top of the atmosphere, approximately 40 million kg annually [3]. The majority of these particles are most closely related to CM chondrites, and thus should carry a few percent organic material by weight, initially. These particles experience severe heating upon atmospheric entry, reaching their peak temperatures at altitudes of >85 km [2] (see also [4] in this volume for more details on atmospheric entry temperatures). Most micrometeorites are melted either partially or completely, indicating that they reached temperatures sufficient to melt silicate, >1600 K [2] [3]. Such strong heating had been assumed to cause complete destruction of the organic content of the particles in this size range.

In recent years, the new field of astrobiology has generated much interest in the relationship of extraterrestrial organic compounds and the prebiotic environment of early Earth. The process of delivering material to habitable planets generates tremendous heat whether it is via micrometeorites or km-sized objects; thus, this step seems to be a potential dealbreaker for a relationship between interstellar or meteoritic organic compounds and the origin of life. However, in recent years the

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questions have been further refined to investigate how infalling material is modified during the delivery process, as opposed to whether this or that molecule can ‘survive’ delivery. For instance, Court and Sephton [1] found that methane evolves from the pyrolysis of carbonaceous chondrite particles.

Here, we report preliminary results on two sets of experiments: 1) atmospheric entry was simulated by flash-pyrolyzing micrometeorite analogs, producing methane and a variety of organic compounds, and 2) heterogeneous chemistry in Earth’s upper atmosphere was simulated with sulfuric acid-catalyzed reactions among two of the pyrolysis products, resulting in the formation of more complex organic compounds.

2 Atmospheric Entry

A fresh fragment from the interior of the Murchison CM 2 carbonaceous chondrite was crushed and sieved to yield 300 μm diameter particles. To reproduce the effects of atmospheric entry encountered by micrometeorites, these particles were flash-heated at 500 K/second to temperatures in excess of 1300 K in a CDS 1000 pyroprobe with heated injector interface. This instrument has been used in pyrolytic analysis of ancient biomacromolecules and extraterrestrial organic solids. Upon release from the solid particle, the pyrolysis products were entrained in a helium stream and deposited on a cold finger (a loop of the GC column immersed in liquid nitrogen). Upon liquid N_2 boil off, the molecular products (pyrolysate) are chromatographically separated on the GC column (a Supleco SPB 50, 50% phenyl-50% dimethyl silicone) employing an Agilent 6890 series GC and analyzed with a HP5972 mass spectrometer.

3.5 wt % of the Murchison meteorite is composed of organic material; of this approximately 30 wt % of these organics are converted into volatiles during flash pyrolysis, the remaining 70 % is a char. The resulting mass spectrum is shown in Figure 1. The majority of the organics were evolved in a temperature range of 500 to 1000 K. The volatile organics appeared to have been completely removed from the particle by a temperature of 1000 K.

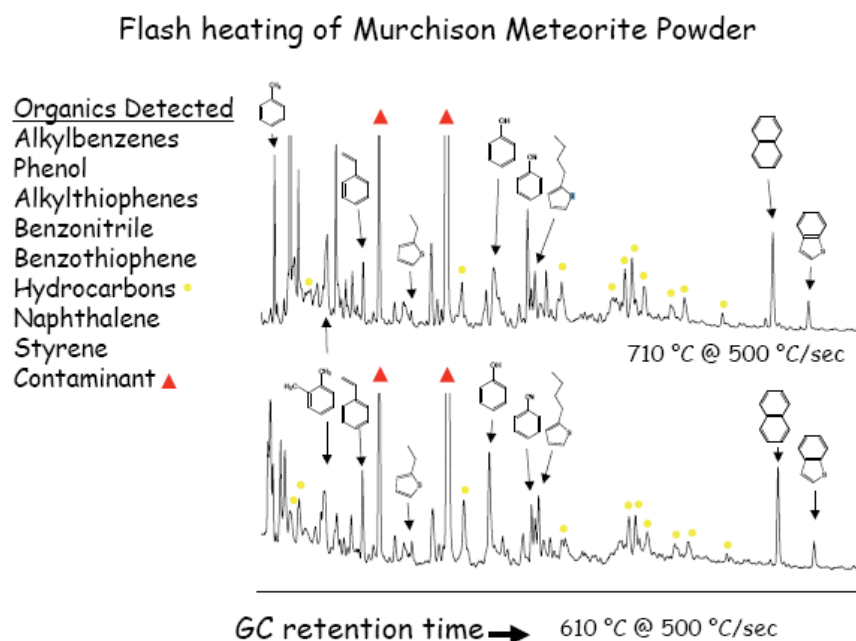


Figure 1. Products evolved upon flash pyrolysis of micrometeoritic analog particles

The compounds that were identified as pyrolysis products included relatively simple compounds including CO, CO₂, H₂O, CH₄, and H₂S. Also evolved from the meteorite during pyrolysis were complex organics, including alkylbenzenes, phenol and alkyl phenols, alkylthiophenes, benzonitrile, benzothiophene, a variety of light hydrocarbons, naphthalene and alkyl-naphthalenes, styrene, and a minor amount of larger polycyclic aromatics including anthracene and phenanthrene. The absolute and relative abundances of these compounds have not yet been quantified.

3 Heterogenous Chemistry in the Upper Atmosphere

Sulfuric acid particles exist in Earth's upper atmosphere, and organic compounds often react strongly with this acid. We have studied the reaction of phenol and styrene, two of the compounds identified in the pyrolysis experiments that are known to independently undergo reactions with sulfuric acid. The sulfuric acid solution was used as a surrogate matrix to mimic upper atmospheric particles.

Theory predicts an acid-catalyzed reaction between phenol and styrene to produce 4-(1-phenylethyl) phenol (shown in Figure 2), and our experiments showed spectral evidence consistent with this pathway (Figure 3). The reaction mixture is compared with 4-cumylphenol which serves as an analog for 4-(1-phenylethyl) phenol, which was not commercially available but has a very similar infrared spectrum. The only difference between these two structures is that 4-cumylphenol has an additional methyl group on the α carbon atom in place of the hydrogen atom. H₂SO₄ concentrations higher than 30 wt% are required to obtain reaction at all temperatures and in a short amount of time. In general, reaction occurs more readily at colder temperatures (5°C compared to 65°C).

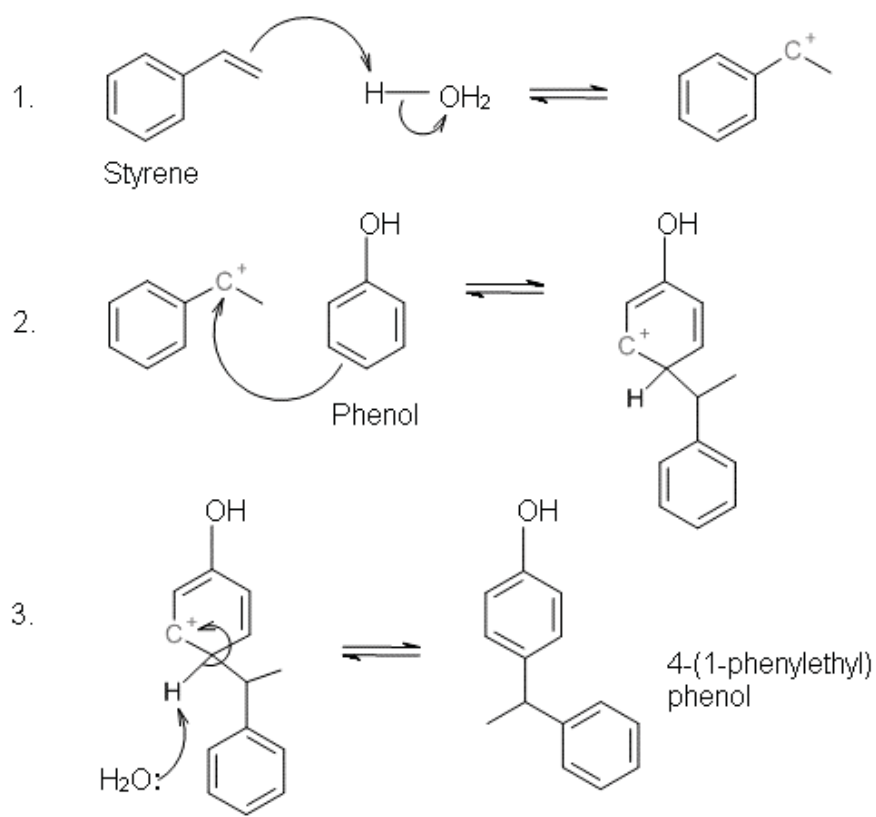


Figure 2. Theoretical acid-catalyzed reaction between phenol and styrene yields 4-(1-phenylethyl) phenol. Note loss of =CH₂ in step 1 and addition of -CH₃ group.

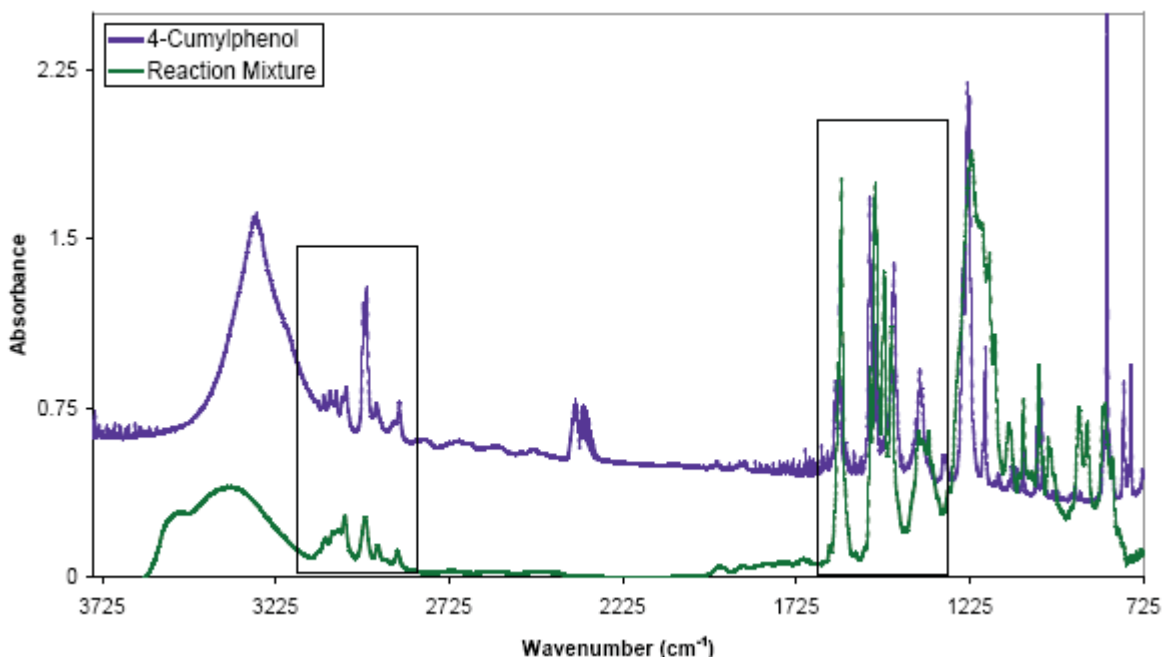


Figure 3. Comparison of 4-cumylphenol IR spectrum (upper curve) with that of the of reaction mixture (lower curve). This reaction mixture was 70wt% sulfuric acid heated to 40°C for 5 minutes and then remained at 20°C for one day. 4-cumylphenol is an analog for the predicted product, 4-(1-phenylethyl) phenol, shown in Figure 2.

4 Summary and Future Work

The fate of organic material entering Earth's atmosphere from space is not well understood. The preliminary results from our experiments show that 1) a wide variety of organic compounds may be released from micrometeorites during atmospheric entry, and 2) these compounds may then go on to react with each other under conditions in the Earth's upper atmosphere. In particular, we found that phenol and styrene are released from flash-pyrolyzed CM chondrite micrometeorite-analogs. We also found that, under conditions analogous to those of the upper atmosphere, phenol and styrene react to produce a compound with a para-disubstituted aromatic ring.

Meteor-derived organic compounds are susceptible to destruction by solar UV, which has a higher flux at altitudes where most of the organic compounds will be released (>85 km). Organic compounds will be destroyed by prolonged exposure to solar UV; this issue is discussed in more detail in Pevyhouse & Kress ([4], this volume). If organic compounds are to persist in the atmosphere, they must be readily mixed to lower altitudes over timescales that are short compared to their photochemical lifetimes. Aromatic compounds are generally more stable to photolysis than are aliphatic hydrocarbons and thus are more likely to participate in heterogeneous chemical reactions leading to greater chemical complexity in the Earth's modern atmosphere.

Future work will entail quantifying the compounds released during entry conditions. Once the abundances these species are measured, they can be incorporated into atmospheric chemical models. The questions of astrobiological interest include investigating the roles that aromatics and light hydrocarbons play in planetary atmospheres. These compounds are strong greenhouse gases, and they also drive smog production in low-O₂ environments. Aromatic compounds also may be important in organic haze production, and they are excellent absorbers of ultraviolet radiation. On the early Earth,

high levels of aromatic compounds from infalling debris may have shielded the prebiotic planetary surface from stellar UV. An understanding of these chemical processes may also be critical to preempting false positives that masquerade as biomarkers in the atmospheres of exoplanets.

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