Organic Synthesis in Experimental Impact Shocks

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Laboratory simulations of shocks created with a high-energy laser demonstrate that the efficacy of organic production depends on the molecular, not just the elemental composition of the shocked gas. In a methane-rich mixture that simulates a low-temperature equilibrium mixture of cometary material, hydrogen cyanide and acetylene were produced with yields of 5 × 10^{17} molecules per joule. Repeated shocking of the methane-rich mixture produced amine groups, suggesting the possible synthesis of amino acids. No organic molecules were produced in a carbon dioxide–rich mixture, which is at odds with thermodynamic equilibrium approaches to shock chemistry and has implications for the modeling of shock-produced organic molecules on early Earth.

At high temperatures (>10,000 K) in shocked gases, reactions are thought to be so rapid that the mixture is in chemical equilibrium. As the gas cools, a temperature is reached at which the reactions become too slow to maintain equilibrium, and the chemical composition of the mixture is quenched or frozen at the equilibrium value determined by the freeze-out temperature (*1–4*). Refinements on this approach have been suggested, notably the assignment of a separate freeze-out temperature for each chemical species (*2, 3*), but the approaches are all equivalent to assuming that reaction rates are infinite at temperatures above the freeze-out temperature and zero below. The problem thus reduces to determining the equilibrium composition of the gas mixture of interest at the freeze-out temperature. The results depend only on the elemental composition of the shocked gas and not on its initial molecular state.

For NO production in Earth's atmosphere, the freeze-out approach gives reasonable results (*1*). However, for fully reducing atmospheres (CH_4-rich) the organic production by shocks (generated by lightning, or cometary or asteroid impact) is not well accounted for by the freeze-out theory (*5–7*). We therefore tested intermediate cases in which key species, such as C, can exist in either a reduced or an oxidized state while maintaining the same C/H/O elemental ratios.

We used a cometary composition as this intermediate case (Table 1). Comets may have influenced the inventory of organic molecules in Earth's primitive atmosphere, and scenarios in which the atmosphere has an elemental composition similar to that in comets are possible (*2*). Although organic molecules are present in comets (*8*), the high-speed impacts are expected to be so energetic that the ensuing fireball destroys virtually all molecular species in the impacting object. As potential analogs of Earth's early atmosphere, we considered impacts into atmospheres where most of the C is in CO_2 versus an atmosphere where about half of it is in CH_4. Free-energy calculations (*9*) indicate that, at low temperatures, CO_2 and CH_4 should be formed in equilibrium mixtures of cometary volatiles, whereas at high temperatures, CO and CO_2 should be the dominant forms of C (Fig. 1). All other organic molecules had predicted mole fractions of $<10^{-6}$.

It is possible to estimate the freeze-out temperature by using numerical models of chemical reactions within the various mixtures (*2, 3*). Freeze-out temperatures between 2000 and 3000 K were determined from studies of NO production by lightning in the terrestrial atmosphere (*1, 4*) and HCN production in reducing mixtures (*2, 3*). For a cometary gas mixture at typical freeze-out temperatures (2000 to 3000 K), C and H are in the reduced form (CO > CO_2; H_2 > H_2O) (Fig. 1). However, there are no organic species present at mole fractions above 10^{-6} in the equilibrium composition (for example, the maximum mole fraction of HCN is 5.3 × 10^{-7} at 2000 K); hence, virtually no production of organic molecules would be predicted by freeze-out calculations.

To test these models, we simulated high-temperature gaseous cometary impacts into a simplified model of Earth's atmosphere for two cometary compositions. The CH_4-containing gas consisted of H_2O, CO_2, CH_4, N_2, and H_2S at a total pressure of 1 bar (Table 2) (*10*). The H_2–CO_2 mixture consisted of two-thirds H_2 and one-third CO_2, by volume. This mixture was designed to provide cometary abundances of C, H, and O without CH_4. The minor constituents, N_2 and H_2S, were not included in the H_2–CO_2 mixture because only the comparison of hydrocarbon production was of interest.

Table 1. Abundances of the biogenic elements in atom numbers normalized to Si = 1 (*25*).

Element	Cosmic	Comets	Carbonaceous chondrites
H	26600.0	30.0	2.0
C	11.7	8.1	0.7
N	2.3	1.4	0.05
O	18.4	18.8	7.5
S	0.5	0.6	0.5
Si	1.0	1.0	1.0

To produce a high temperature shock wave in the laboratory, we used the focused beam of a 1.06 μm Nd-YAG (yttrium-aluminum-garnet) high-power pulsed laser (*11*). The initial plasma temperatures were in excess of 10,000 K, but the expanding gases rapidly cooled as the shock wave propagated outward from the initial volume (*12*). On the basis of measurements of the emission of visible light from the plasma (*6, 13*), we determined that the plasma cooled in about 100 ns. Expansion of the high-temperature gas took ~1 to 2 μs. Although these times are shorter than the typical shocks from an entry shock by an impact, 10 s (*14*), or lightning, 22.5 μs (*13*), spectral comparisons (*13*) show that the laser-induced plasma provides a reasonable laboratory simulation of the high-temperature conditions associated with strong heating in which gases are heated to >10,000 K and therefore achieve chemical equilibrium (*15*). The laser-induced plasma probably does not provide an accurate simulation of the weaker shocks associated with cometary

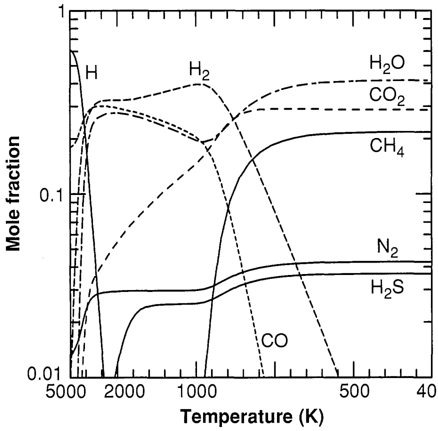

Fig. 1. Thermodynamic equilibrium mixture of cometary volatiles as a function of temperature at a pressure of 1 bar. Elemental ratios are given in Table 1, except that 10% of the O_2 has been removed to account for oxides in the rock fraction of the comet. At typical quench temperatures of 2000 to 3000 K, the gas mixture is reducing (for example, H_2 and CO); however, organic species in the equilibrium mixture occur at levels $<10^{-7}$. Units on the horizontal axis are in inverse temperature.

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impactors that enter with velocities less than several km s^{-1} such as secondary ejecta from a comet impact.

The gases produced in the CH_4-containing mixture were determined by gas chromatography–mass spectrometry (GC-MS) (*16*). The efficiency of formation for organic molecules is high in the mixture containing CH_4 and is comparable to the formation efficiency of NO in lightning, $\sim 10^{17}$ molecules J^{-1} (Table 2) (*1*). We surmise that most of the O and H released from the formation of the organic compounds from CO_2 and CH_4 reformed as water, leaving excess H_2. Hydrogen was detected at $\sim 10^{17}$ molecules J^{-1}. Ammonia (NH_3) was not detected, but its presence may have been masked by CH_4. No carbon compounds larger than C6 were detected. In the H_2–CO_2 mixture, the reaction is effectively the transfer of O from CO_2 to H_2, producing H_2O and CO in equimolar quantities. The production efficiency of about 0.5×10^{17} molecules J^{-1} and these products correspond to the predicted equilibrium composition at about 2500 K (Fig. 1). A solid residue also was produced when the CH_4 gas mixture was subjected to long exposure times (*17*).

Two regions were evident in the shocked region in our experiments: (i) a core region where the gas was subjected to high temperatures and pressures, and times sufficient to dissociate all molecules, and (ii) a large outer region where the gas was heated sufficiently to dissociate many molecular species but the gas was never so hot that the most stable species were dissociated. Organic material was produced from the CH_4-containing mixture, possibly due to exposure to ultraviolet (UV) light (*18*) or photochemical reaction with cooler gas. UV light may trigger the formation of organic molecules from CH_4 in regions sufficiently far from the high-temperature core that the shock wave is too weak to destroy them when it expands to that distance. Alternatively, CH_4 in the ambient gas may react with shock-produced species as the gas cools. As the shock wave expands and weakens, the temperatures may be high enough to promote CH_4 reactivity without pyrolyzing the organic molecules produced. Many of the products (Table 2), especially C_2H_2 and C_2H_6, are known to be photochemical products of CH_4 photochemistry (*19*).

Table 2. Mass peaks resulting from initial shock heating of cometary volatiles composed of 42% H_2O, 29% CO_2, 22% CH_4, 4.3% N_2, 3.7% H_2S and production as molecules per joule of plasma energy.

Mass	Probable compound	Production
26	C_2H_2	5×10^{17}
27	HCN	5×10^{17}
76	C_6H_4	5×10^{17}
31	CH_3NH_2	1×10^{17}
25	C_2H	1×10^{17}
24	C_2	5×10^{16}
46	$C_2N_2H_4$ or CO_2H_2	5×10^{16}
60	$C_2O_2H_4$	5×10^{16}
78	C_6H_6	5×10^{16}
64	S_2	5×10^{16}
30	HCHO	2×10^{16}
48	CH_3SH	1×10^{16}
30	C_2H_6	2×10^{14}
28	C_2H_4	5×10^{14}

The comet impact, lightning, and the laser-induced plasma simulation represent situations in which a hot gas is suddenly introduced into a larger and cooler atmosphere. This situation causes a shock wave to propagate outward, engulfing the ambient gas. As the shock wave and hot core expand, they cool and engulf an ever larger volume of ambient gas that is then heated by mixing and radiation.

The low-temperature equilibrium gas mixture of cometary volatiles contains CH_4 (Table 1). Although the composition of Earth's early atmosphere is uncertain, an early CH_4-containing atmosphere is consistent with the reducing nature of the accreting material (*2*) as well as degassing during the accretional phase (*2*, *20*). However, CH_4 has a short lifetime in the atmosphere because of photochemical processes and, in our cometary scenario, a CH_4-containing atmosphere would only be supported during the period of accretion when the flux of CH_4 by comets would be greater than the photochemical losses. Shielding of UV by organic soot and haze particles may have extended this period.

In a CH_4-containing atmosphere, additional shocks produced by further cometary infall or by lightning could produce organic molecules (Table 2) (*21*). Thus, even if the incoming organic material in a comet was destroyed in the impact, shock processing of the cometary gases residing in the atmosphere could resynthesize organics. Because of the high production efficiencies (Table 2), we conclude that comet impacts could have been a significant source of organic material in an atmosphere containing CH_4 (*22*). Conversely, if atmospheric processes had already oxidized the carbon in the atmosphere to CO or CO_2 before the impact, then the result might be quite different even though the atom fractions of C, H, and O had not changed. Little or no organics would have been produced. Thus, the molecular composition of the atmosphere, as well as the atomic fractions, determine the outcome of the impacts.

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10. The CH_4-containing mixture was 42% H_2O, 29% CO_2, 22% CH_4, and 4.3% N_2. The gases other than water were obtained as premixed research-grade gases. This gas was added to the correct amount of distilled water in a 250-ml glass flask to achieve the final mixture. The sample flasks and the controls were placed within an oven held at 80°C, such that all the water was in vapor form.
11. Typically, the beam contained ~0.2 J in a pulse of ~15 ns, repeated 10 times a second (*6*). A plasma formed when the laser beam was brought to a focus, as first reported by P. D. Maker, R. W. Terhune, C. M. Savage [in *Proceedings of the 3rd International Conference on Quantum Electronics*, Paris, 11 to 15 February 1963 (Columbia Univ. Press, New York, 1964), vol. 2, pp. 1559–1576]. See also Yu. P. Raizer, *Sov. Phys. Usp.* **8**, 650 (1966); L. R. Radziemski, T. R. Loree, D. A. Cremers, N. M. Hoffman, *Anal. Chem.* **55**, 1246 (1983); D. D. Davis, G. R. Smith, W. A. Guillory, *Origins Life* **10**, 237 (1980). The spectral properties and optical emission of the laser-induced plasma have been characterized (*6, 13, 23, 24*). For gas-phase analysis, we used a 4-min exposure. The total energy deposited is sufficient to heat only about 15% of the gas to a freeze-out temperature of 2500 K. However, some experiments were conducted in which the exposure time was increased to 20 min to allow for maximal processing of the mixture and the production of a solid residue. The laser output was directly measured with a bolometric power meter. None of the gaseous species in the experiment caused significant absorption at the 1.06-μm laser line over the short pathlengths (1 cm) used. The efficiency with which this power was converted to plasma energy was determined by direct measurement of the total power deposited in the test chamber as described (*24*).
12. Using spectroscopy, we characterized the free electron concentration and gas temperature as the plasma cooled (*13*). The electron density dropped from 7×10^{17} cm^{-3} at 0.6 μs after ignition to 0.9×10^{17} cm^{-3} at 4.0 μs after ignition. The electron temperature dropped from 17,000 to 12,000 K over this same interval.
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15. Spectral comparison of the temperature and pressure history of the laser plasma and natural lightning (*12, 13*) indicated that at temperatures near the freeze-out (2000 to 3000 K) the trajectories on a pressure-temperature diagram are similar.
16. The CH_4-containing mixture products were determined with a Hewlett-Packard model 5992 GC-MS, except for ethane and ethylene, which were detected with a gas chromatograph with a metastable ion-drift detector. The mass difference between CO and N_2 could not be resolved, so CO production could not be determined. Analysis was by GC-MS and by direct MS. Hydrocarbon compounds with a mass of >27 were difficult to distinguish because of the large amount of other gases present in the original mixture. The H_2–CO_2 mixtures were analyzed with a Varian 9600 gas chromatograph. Taking into account the variation in the amount of water entered into the sample and variations in the laser beam energy and flask transmission, we conservatively estimated that our values are accurate to a factor of 2.

Improved identification could be achieved if the parent gases are removed by cryogenic cooling. Samples and controls were kept shielded from sunlight and room light. No measurable production of organics was found in the controls.

17. The solid residue was analyzed by solution in boiling dichloromethane and in methanol. No organic material was detected at a level of 1 ppm in the dichloromethane. The methanol solution, examined with a Fourier Transform Infrared Spectrometer (IBM model 32), indicated the presence of soluble organic matter. Infrared absorption bands were identified at 2922, 2855, and 1450 wavenumbers, indicating the presence of aliphatic hydrocarbons; at 1516 wavenumbers, indicating a small amount of aliphatic amine; at 1636 wavenumbers, indicating an amide group; and at 1117 wavenumbers, indicating the possible presence of alcohol groups. We could not accurately determine the yield of the solid residue because of the long exposure time required to produce this material and the resulting reprocessing of products. However, based on the exposure time (20 min) and product amount (determined to be about 0.01 mg on the basis of concentrations in solution), we can estimate its yield at about 1% of the yield of the major hydrocarbons. An x-ray fluorescence spectrum of the solid residue showed a strong sulfur line, indicating incorporation at the few percent level in the solid residue.
18. We estimated the importance of UV production, using the results of experiments in which the shock is isolated from the parent mixture by a UV transparent window (6). Yields of the main photolysis products with UV-only compared to yields with complete shocks were: 1 to 4% C_2H_2, 10 to 20% C_2H_6, and 0.1 to 1% HCN. Our results correspond to similar yields for the UV production, ≈1 to 10% of the total shock production is due to UV.
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22. We can compare the expected yields for organics on early Earth with the other main production mechanism, solar UV light. C. Chyba and C. Sagan [*Nature* **355**, 125 (1992)] estimate that the solar UV produces 3×10^8 kg year^{-1} in a neutral atmosphere and 2×10^{11} kg year^{-1} in a reducing atmosphere. For our CH_4-containing mixture and using the atmospheric shock deposition rate estimated by Chyba and Sagan of 10^{17} J year^{-1}, we find an organic production of 3×10^{10} kg year^{-1}. For the lightning rate of Chyba and Sagan, 10^{18} J year^{-1}, the organic production is 3×10^{11} kg year^{-1}.
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Giant Piezoelectric Effect in Strontium Titanate at Cryogenic Temperatures

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Piezoelectric materials have many applications at cryogenic temperatures. However, the piezoelectric response below 10 kelvin is diminished, making the use of these materials somewhat marginal. Results are presented on strontium titanate ($SrTiO_3$), which exhibits a rapidly increasing piezoelectric response with decreasing temperature below 50 kelvin; the magnitude of its response around 1 kelvin is comparable to that of the best materials at room temperature. This "giant" piezoelectric response may open the way for a broad class of applications including use in ultralow-temperature scanning microscopies and in a magnetic field–insensitive thermometer. These observations, and the possible divergence of the mechanical response to electric fields at even lower temperatures, may arise from an apparent quantum critical point at absolute zero.

The phenomenon of piezoelectricity, as a solid-state method for converting electrical signals into mechanical motion, has become ubiquitous in its applications in the laboratory as well as in everyday life. Its elegant simplicity is evident in such varied uses as the beeping of a watch and the ultrasensitive micropositioning required to arrange individual atoms on a surface. However, it is not without limitations. In particular, the piezoelectric response is typically reduced by orders of magnitude at cryogenic temperatures. We have found an important exception to this in the crystal $SrTiO_3$ (STO), for which the piezoelectric response grows at low temperature and at 1.6 K is comparable to that of the best materials at room temperature.

We present results from measurements of the electric field–induced strain in single crystals of STO in the temperature range $T = 1.6$ to 50 K. This material is one of the most widely studied in condensed-matter physics, exhibiting a variety of phenomena including structural phase transitions (*1*) which have been calculated recently from first principles (*2*), the rare phenomenon of second sound (*3*), and the identification of a low-temperature quantum paraelectric (QPE) ground state by Müller and Burkard (*4*). It is the latter which underlies the phenomena in our investigations.

The electric field–induced (*5*) and pressure-induced (*6*) strain in STO has been investigated since the early 1960s, but the observations were confined to a few temperatures and voltages. In this work, we have mapped out a full surface in voltage and temperature, which reveals behavior much richer than previously thought (Fig. 1). Perhaps the most important feature of the data is the strong increase in the magnitude of the electric field–induced strain S as T is decreased. The strain S is the relative change in length, $\Delta\ell/\ell$ along $\hat{x}$ for a field $\mathbf{E} = E\hat{z}$. By contrast, standard piezoelectric ceramics such as lead zirconate titanate (PZT) would exhibit a strain of the order 10 microstrain at our lowest temperature for the same sample geometry. Further, the strain in PZT decreases as T is lowered, whereas the strain in STO increases.

The experiments were performed on a single-crystal substrate of STO, 10 mm by 10 mm by 0.75 mm, from Princeton Scientific. The impurities were determined by the manufacturer (*7*). We measured S using a foil strain gauge from Omega Engineering (model SG-LY11). The gauge was bonded with cyanoacrylate (Omega) after the faces of the crystal had been coated with 500 Å of chrome. Calibration of the gauge was based on measurements on commercially available PZT with typical strain versus temperature characteristics. Thus, although the precision of the gauges is better than 10^{-7} strain, the accuracy is only about 20%.

At low voltages, the strain is quadratic in the voltage (Fig. 2), characteristic of a paraelectric (PE). In this regime, S for a field E is given by

$$S_{ij} = R_{kij}E_k^{\,2} \qquad (1)$$

where the coefficient of electrostriction, $\mathbf{R}$, is a fourth-rank tensor, with $i, j = 1$ to 3 and $k = 1$ to 6 in a double-index form (*8*). Above a crossover voltage V_c associated with a crossover field E_c (voltage is the measured quantity and it is simply related to the field E through the crystal thickness, $t = 0.75$ mm), the strain is linear in field, characteristic of a piezoelectric, with

$$S_{ij} = d_{kij}E_k \qquad (2)$$

where the piezoelectric coefficient, $\mathbf{d}$, is a third-rank tensor (*8*), with $i, j, k = 1$ to 3. We always applied E_3 and measured R_{311} and d_{311} (*9*).

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