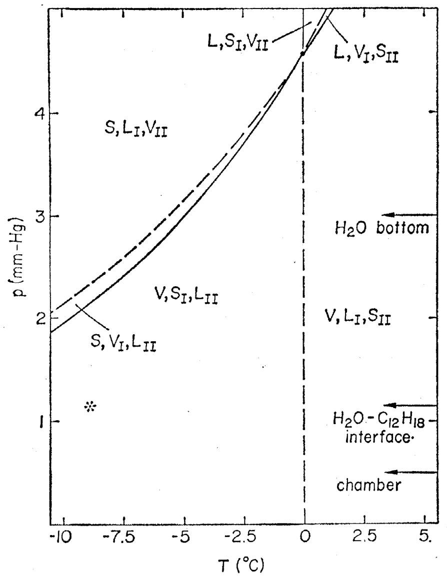

Fig. 3. Phase diagram showing significant system locations. The asterisk indicates the state of the system at the H_2O-$C_6H_3(C_2H_5)_3$ interface at the onset of freezing.

low pressures), the chamber pressure was reduced to 0.5 mm-Hg. At this time the water and oil were at temperatures of 16.7°C and 17.8°C, respectively. The pressure in the water at the water-triethylbenzene interface was only 1.1 mm-Hg, and at the bottom of the beaker the pressure was only 3.0 mm-Hg; both of these values are well below the triple point pressure of 4.6 mm-Hg. The water was in state L_I, superheated with respect to the equilibrium vapor phase (Fig. 1b). Throughout the rest of the experiment the chamber pressure was maintained at 0.5 mm-Hg.

The temperatures of the water and the oil were slowly reduced. The water did not freeze at 0°C; instead it went through the stability transition $L_I \rightarrow L_{II}$ (Fig. 1b) and continued to cool to −9.4°C where rapid freezing commenced at the water-triethylbenzene interface and at the beaker walls. The temperature of the ice-water mixture rose abruptly (within 6 seconds) to −2.8°C (Fig. 3). Subsequent freezing farther from the interface proceeded more slowly and the temperature increased to −0.6°C in about 3 minutes, during which time the oil temperature rose from −15°C to −7.8°C (*3*). Some 3 minutes after freezing commenced ice-encrusted bubbles began to grow in the water-ice mixture near the bottom of the beaker, and this volumetric expansion caused the water to break through the thin ice crust at the water-triethylbenzene interface. These bubbles were held in the ice-water matrix near the bottom of the beaker and their growth was sufficiently slow so that the water was able to rise gradually above the ice crust at the original water-triethylbenzene interface and to displace the triethylbenzene upward without disrupting it. This upward displacement of the triethylbenzene is evidence that the ice which formed at the water-triethylbenzene interface did not pressurize the system above the chamber pressure. The experiment was terminated when the water had risen 1 cm above its original level. After pressurization of the system, the bubbles collapsed and the water returned to near its original position (some bubbles frozen into the coherent ice mass that had formed at the bottom of the beaker remained after pressurization).

Ice, formed at the triethylbenzene-water interface, was in state S_I, superheated with respect to the equilibrium vapor, whereas the liquid that remained was in state L_{II} (Fig. 1c), supercooled with respect to the ice in state S_I but also superheated with respect to vapor in state V. Vapor either in state V or V_I was contained in the ice-encrusted bubbles that formed subsequent to the freezing. We believe that in the experiment reported here a superheated liquid L_{II} has been made to freeze to the superheated solid S_I, a hitherto unobserved phase transformation.

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3. The use of the glass bell jar vacuum chamber allowed us to observe the system throughout the course of the experiment. Thus, even though there was only a single thermocouple below the H_2O-$C_6H_3(C_2H_5)_3$ interface, the growth of ice in different parts of the system could be seen.
4. We thank the staff of the Jet Propulsion Laboratory, California Institute of Technology, Pasadena, for the use of their vacuum equipment. We thank D. Ross, J. Stoker, W. Andrews, P. Miller, and L. Short of the Environmental Test Laboratory of the Jet Propulsion Laboratory for their invaluable aid and cooperation. Supported in part by NSF grant Ga-10167. Publication No. 810, Institute of Geophysics and Planetary Physics, University of California, Los Angeles.

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Shock Synthesis of Amino Acids in Simulated Primitive Environments

Abstract. *A mixture of gases roughly simulating the primitive terrestrial atmosphere has been subjected to shock heating followed by a rapid thermal quench. Under strictly homogeneous conditions there is a very high efficiency of* 5×10^{10} *molecules per erg of shock-injected energy for production of alpha-amino acids. Calculations suggest that rapid quenching bypasses the usual thermochemical barrier. The product of energy flux and efficiency implies the unexpected conclusion that shocks occurring on atmospheric entry of cometary meteors and micrometeorites and from thunder may have been the principal energy sources for prebiological organic synthesis on the primitive earth.*

A wide variety of energy sources are effective in generating α-amino acids (among many other organic compounds) from simulated primitive environments; the atmosphere of precursor gases may apparently have any composition, provided only that it is reducing and that the atoms H, N, O, and C are present (*1, 2*). There has heretofore been no report of simulated prebiological organic synthesis in shock tubes. Such syntheses may be of importance because (i) the composition and temperature of the gas mixture, the duration of activation, and the rate of quenching can be controlled; (ii) the significant kinetic reactions occur under strictly homogeneous conditions, since the sample is heated gas dynamically while the tube walls are cold; and (iii) as discussed below, the product of energy available from shock sources on the primitive earth and the efficiency of synthesis suggests that shock excitation may have been a major source of primordial organic molecules.

The single-pulse shock tube used for these experiments consisted of a Pyrex low-pressure (driven) section of uniform bore, 2.5 cm in inner diameter and 175 cm long, and a brass high-pressure (driver) section, 2.5 cm in inner diameter and 45 cm long. These were separated by 3-mil Mylar diaphragms which were burst (thus initiating the shock) when the helium driver gas pressure was raised to about 8.1 atm (*3*). Pressure traces were recorded with a dual-beam oscilloscope with one beam operating at a total scan time of 100 μsec and the other at a total scan time of 5 msec, from which the shock speed and duration were calculated.

Table 1. Experimental conditions for shock synthesis. Average dwell periods in reflected shock regime were $\simeq$ 500 μsec. For group A the test gas was argon plus water. For groups B and C the test gas was 3.3 percent (by weight) CH_4, 11 percent C_2H_6, 5.6 percent NH_3, plus H_2O (as described in the text); the major constituent was argon.

Shock No.	(Estimated) H_2O pressure (torr)	Total initial pressure (torr)	Incident shock speed (mm/μsec)	Approximate reflected shock temperature* (°K)
		Group A		
1	25	50	1.18	2000
2	22	47	1.18	2000
3	12	32	1.33	3000
		Group B		
4	19	69	1.08	1600
5	10	35	1.30	3000
6	10	35	1.30	3000
		Group C		
7	20	110	0.95	1000
8	7	30	1.30	3000
9	5	20	1.42	3500
10	3	15	1.42	3500

* Estimated on the basis of no reaction, on the assumption that argon was the driven gas. Actual sample temperatures are several hundreds of degrees lower.

The reaction mixture, prepared in a large glass bulb, consisted of 3.3 percent (by weight) CH_4, 11 percent C_2H_6, and 5.6 percent NH_3 (Matheson "pure" grade, used without further purification), diluted with Matheson ultrapure argon. We do not believe the results would be significantly affected by many other choices of reduced gases (*1, 2*). A second glass bulb was partly filled with distilled water and degassed several times under vacuum with the water alternately frozen and heated.

The glass section of the shock tube was cleaned 25 times with toluene and ethanol. After each cleaning the paper towel was checked with ninhydrin spray for the presence of amino acids; all tests were negative. With a heating tape the temperature of the driven section was raised to approximately 80°C and the driven section was pumped to below 10^{-4} torr for 5 hours. Water vapor at pressures of 5 to 25 torr was then introduced into the *driven* section from the water reservoir bulb attached to one of the valves located at the terminal end of the test section, and then the reaction mixture was introduced from the opposite end of the driven section. Sample pressures ranged from 10 to 90 torr. Two minutes were allowed for partial mixing. The helium driver gas was then introduced slowly until the diaphragm burst, sending the shock wave down the tube. As successive sections of the sample gas are traversed by the incident shock front their temperatures rise sharply, in 10^{-8} second to between 1000° and 2000°K (depending on the shock speed). Because of conservation of momentum, the wave reflected from the terminal plate consists of another compression shock; thus additional heat is supplied to the sample gas (2000° to 4000°K) and the sample gas is additionally compressed to a net density approximately six times the original density. When the reflected shock wave meets the now somewhat diffused boundary region between the driven and the driver gases, there is a sharp drop in pressure and temperature. Quenching is augmented when the length of the *driver* section is adjusted so that the expansion wave reflected from the opposite end of the tube simultaneously arrives at this intersection. Cooling rates in the range of (0.5 to 1.0) $\times$ 10^6 °K sec^{-1} result, depending on the care taken with this "tuning." The dwell periods for the reaction, during which the mixtures are subjected to the reflected shock temperature (for this tube) as determined by the shock speed, ranged from 500 to 100 μsec. The incident and reflected equilibrium shock temperatures are calculated from the equations for the conservation of mass and energy, the thermodynamic functions of the reaction mixture, and the measured shock speed.

As rapidly as one can move, after initiating the shock, the valve between the terminal end of the shock tube and the previously evacuated sample-collecting bulb is opened. For these experiments the sample-collecting bulb was a 2-liter glass vessel into which had been placed 10 ml of 0.1*N* HCl (degassed). After the shocked and quenched gas sample had been collected, the bulb was detached from the tube and was vigorously shaken; the walls were washed by slowly rotating the bulb. The bulb was then evacuated, reattached to the test section, and the next run initiated. A series of three shock samples was obtained for each range of shock speeds and the product samples were collected in one bulb. This solution was then analyzed for amino acids by paper chromatography, with *n*-butanol, methanol, water, and ammonia in the ratio of 10:10:5:2 by volume, respectively, and by column chromatography in an amino acid analyzer.

Ten shocks were made, covering the range of compositions and shock speeds summarized in Table 1. Three control runs (group D) were obtained with the reaction mixture used for groups B and C. For group D, the sample was introduced into the driven section in the usual manner, was allowed to remain in the shock tube for 5 minutes, and then slowly was pushed into the sample bulb by a stream of helium. The mixture had a residence time of about 5 minutes at 380°K. Group A shocks also constitute a control. No amino acids were detected in groups A or D. The absence of amino acids in group A runs demonstrates that the shock tube was clean"; that is, the (hydrocarbon-ammonia-water) mixture is necessary for amino acid production. The absence of amino acids in group D runs demonstrates that shock heating is essential; a 5-minute exposure of the ingredients to a temperature of 380°K is not sufficient to produce amino acids. In groups B and C amino acids were found in the following concentrations (in micromoles per 10 ml): group B contained glycine, 73; alanine, 34.5; valine, 0.55; and leucine, 0.105; group C contained glycine, 62.5; alanine, 17.6; valine, 3.25; and leucine, 0.27. Yields calculated for group B were surprisingly high; 36 percent of the ammonia present was converted to amino acids. This demonstrates direct amino acid production initiated by shocks under strictly homogeneous conditions, with all constituents in the gas phase.

Thermochemical considerations place strict limits on the possible processes. Because of the thermodynamic properties of the reactants and products, one is forced to conclude that the observed high production efficiency is a consequence of the thermal history of the shock sample, that is, the high-temperature pulse during which the reagents are partially fragmented must be followed by a rapid quench, during which the radicals react with the remaining reagents in a chain mechanism. The essential reunification steps occur with relatively low activation energies. The high-temperature thermodynamic barrier is thus bypassed.

The equilibrium compositions of systems which consist of C, H, O, N, S, and other elements indicate (*4*) that at high temperatures the relative concentrations of complex species are very low. The relative concentrations of the four amino acids found in this study are close to the mole fraction ratios of the radicals H, CH_3, $(CH_3)_2CH$, and $(CH_3)_2CH{-}CH_2$ calculated at equilibrium, around 2000°K (*5*). The corresponding ratios are $H/CH_3 \simeq 1.5$, $CH_3/C_3H_7 \simeq 40$, and $CH_3/C_4H_9 \simeq 800$. In experiment B the ratios of the amino acids are glycine/alanine = 2.1, alanine/valine = 63, and alanine/leucine = 350. These rough comparisons indicate that, even though thermodynamic relations do impose a barrier for α-amino acid production and condensation if one insists on isothermal processes, no such restriction is present in precursors marked by rapid quenching.

To place the prebiological synthetic role of shock waves in context, we consider the following rough estimates of relative efficiencies. For the shocks used we estimate that the energy input to the test sample was (4 to 5) $\times 10^{11}$ erg $mole^{-1}$. Since only 5×10^{-4} mole of reagents was present, the rest being argon, these reactants absorbed $\simeq 2 \times 10^8$ ergs, which produced 3.7×10^{-5} mole of amino acids, that is, 2.2×10^{19} molecules, thus implying 5×10^{10} molecules per erg of shock-injected energy. In contrast, the quantum yield for ultraviolet photoproduction of α-amino acids under similar conditions is about 10^{-6}, or less if mercury sensitization is not employed (*6*). This corresponds to $\sim 10^5$ molecules per erg of absorbed long-wavelength ultraviolet light. The efficiency advantage of shock excitation over ultraviolet excitation thus appears to be some six orders of magnitude.

To compare the overall significance of shock and ultraviolet excitation as primitive energy sources we must compare the absolute energies available. One obvious source of shock waves on the primitive earth, comparable in many respects to those produced in our experiments, is hypervelocity impact by cometary meteors and micrometeorites, which dissipate their kinetic energy high above the earth's surface. There are many more orders of magnitude of kinetic energy available in such small objects which do not reach the surface at hypersonic velocities. Hochstim (*7*) has suggested that meteorites, especially large ones, might have contributed to prebiological organic synthesis. Above an altitude of some 90 km, most cometary meteors and micrometeorites have been either completely ablated or thermalized so that the remnants float down to the surface like a fine rain (*8*). A representative and conservative mass flux for the primitive earth is 2×10^{-14} g cm^{-2} sec^{-1} with arrival velocities of some 35 km sec^{-1} (*9*). The corresponding energy flux is $\sim 10^{-1}$ cal cm^{-2} $year^{-1}$ (*10*). An additional source of shocks on the primitive earth is thunder; we wish clearly to distinguish between synthesis in the lightning leader, where at 2×10^4 °K no synthesis occurs, and synthesis in the resulting cooler shock wave. If we assume a rate of electrical discharge on the primitive earth similar to that on the contemporary earth (*11*), and if we assume the usual value of some 70 percent of the electrical energy appearing as the accompanying pressure wave, there is an additional energy source of ~ 1 cal cm^{-2} $year^{-1}$.

Considering the conservative nature of our assumptions, a total shock flux on the primitive earth of ~ 1 cal cm^{-2} $year^{-1}$ does not seem unreasonable. By comparison, the total energy available as ultraviolet light on the primitive earth, at wavelengths shorter than about 3000 Å where some organic photochemistry can be expected, is computed (*2*, p. 238; *12*) from models of the evolution of the sun to be $\sim 10^3$ cal cm^{-2} $year^{-1}$. Accordingly, ultraviolet light was $\sim 10^3$ times more abundant than shock waves on the primitive earth; but shocks are 10^6 times more efficient than ultraviolet light in producing amino acids. The only other energy sources of importance (*11*) appear to be the leader in lightning discharges and volcanic thermal activity. In the first case, temperatures are generally too high for synthesis, and in the second the synthesized molecules are left for a significant time in the high-energy region. The time factor is probably also the principal reason for the low quantum yields for ultraviolet photoproduction. We are thus led to the unexpected conclusion that cometary meteors, micrometeorites, and thunder were the principal energy sources for prebiological organic synthesis by a factor of perhaps 10^3.

The high-pressure shocks of meteors that reach the sea provide an interesting environment for anhydrocopolymerization of amino acids and other monomers which do not readily polymerize in water in the absence of special condensing agents. On the basis of the numbers presented above, it follows that $\sim 10^{10}$ organic molecule cm^{-2} sec^{-1} were produced by shocks on the primitive earth. If the mean molecular weight of synthesized molecules is ~ 100, the production flux is $\sim 10^{-12}$ g cm^{-2} sec^{-1}. For a primitive reducing atmosphere lasting 10^9 years, a total production of organic molecules of ~ 30 kg cm^{-2} is implied. This quantity of carbon is quite comparable to that present as carbonate sediments in the earth's crust, thus suggesting that a major fraction of the present crustal carbon on the earth was once in the form of organic compounds. Were all this organic matter to have survived and to have been dissolved in oceans of contemporary depth and extent, a 10 percent (by weight) solution of organic compounds would result. Even with efficient loss mechanisms it appears that shock production of organic molecules may have played a significant role in the origin of life. It is also not out of the question that shock synthesis of organic compounds might have some practical contemporary applications, as in the generation of foodstuff.

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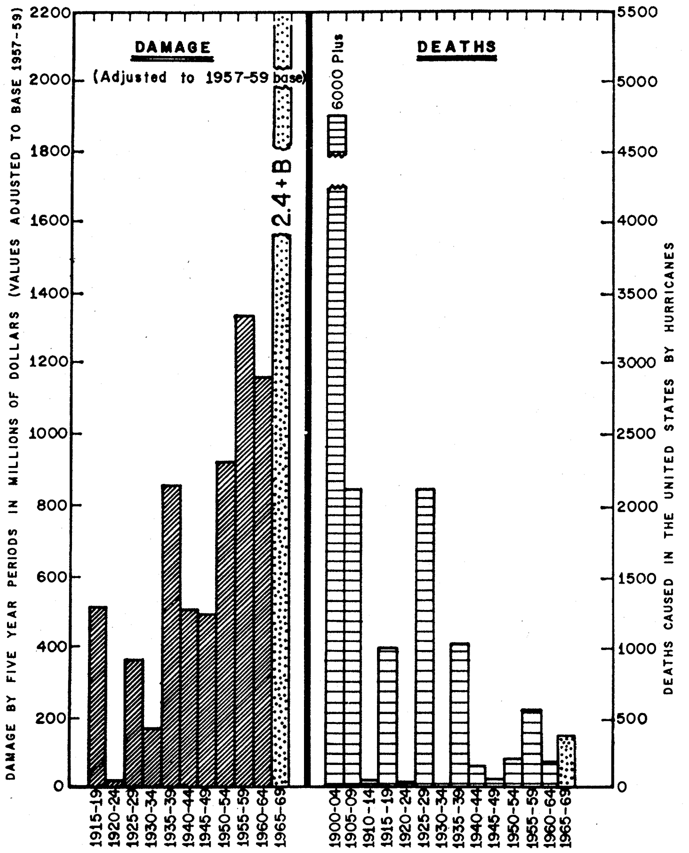
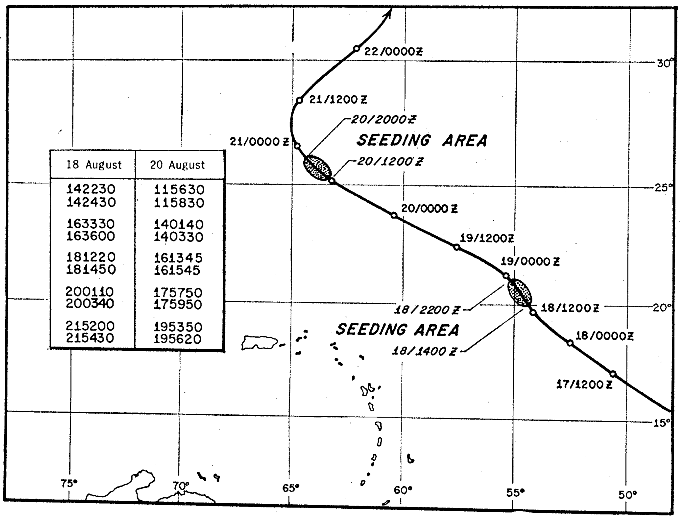
Hurricane Debbie Modification Experiments, August 1969

Abstract. *Maximum winds in Hurricane Debbie, August 1969, decreased after modification experiments by Project Stormfury. Clouds surrounding the center of Debbie were seeded with silver iodide particles five times at approximately 2-hour intervals on both 18 and 20 August. Before the first seeding on 18 August, the maximum speed of winds at 3600 meters was 182 kilometers per hour, but, 5 hours after the fifth seeding, these winds decreased to 126 kilometers per hour. On 20 August, the corresponding change was from 183 to 156 kilometers per hour. Analyses of the data suggest that the storm was modified.*

Project Stormfury conducted modification experiments on Hurricane Debbie on 18 and 20 August 1969. These experiments were the first performed on hurricanes since 1961 and 1963 (*1*) and the first in which a storm was ever seeded more than once per day. Debbie was seeded five times during 8 hours on each of the 2 days. This report presents preliminary analyses of the data collected in the Hurricane Debbie modification experiments.

R. H. Simpson proposed in 1961 that hurricanes might be modified by introducing freezing nuclei into the massive clouds surrounding the center of a hurricane. At about the same time Pierre St. Amand and his associates at the Navy Weapons Center, China Lake, California, developed pyrotechnic generators, which made it practical to introduce very large quantities of silver iodide into clouds within a few minutes. Groups from the Weather Bureau and the Navy experimented on Hurricane Esther with a single seeding on each of 2 days in September 1961. Project Stormfury was formally organized in 1962 with R. H. Simpson as the first director. In August 1963, the experiment with a single seeding per day was repeated on each of 2 days for Hurricane Beulah. The results of these earlier experiments have been reported by Simpson and Malkus (*1*) and were encouraging but inconclusive. A multiple seeding experiment was designed under the leadership of Joanne Simpson, director of the project for 1965–66. During the years 1965–68 no hurricane occurred in a place suitable for experimentation. Research on hurricanes, both theoretical and experimental, con-





18 August	20 August
142230 142430	115630 115830
163330 163600	140140 140330
181220 181450	161345 161545
200110 200340	175750 175950
215200 215430	195350 195620

Fig. 1 (left). Trends in losses from hurricanes in the United States summarized by 5-year periods. Damage statistics have been adjusted to the 1957–59 base of the Department of Commerce composite cost index for construction. The adjusted total for 1965–69 exceeded \$2.4 billion, which also exceeds the vertical scale of the chart. Fig. 2 (above). Track of Hurricane Debbie, August 1969. Seeding areas on 18 and 20 August are indicated on the track; Z indicates Greenwich Mean Time. The inserted table contains a list of the times of seedings in hours, minutes, and seconds (G.M.T.).