'THUNDER': SHOCK WAVES IN PRE-BIOLOGICAL ORGANIC SYNTHESIS

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Abstract. A theoretical study of the gas dynamics and chemistry of lightning-produced shock waves in a postulated primordial reducing atmosphere was conducted. It was shown that the conditions are similar to those encountered in a previously performed shock-tube experiment which resulted in 36% of the ammonia in the original mixture being converted into amino acids. The calculations gave the (very large) energy rate of about 0.4 cal/cm^2/yr available for amino acid production, supporting previous hypotheses that 'thunder' could have been responsible for efficient large scale production of organic molecules serving as precursors of life.

A very high energy-efficiency was recently demonstrated by Bar-Nun *et al.* (1970) for the production of amino acids behind shock waves in a postulated primordial reducing atmosphere. The essential features of the shock synthesis which are responsible for the high efficiency are a rapid heating of the gas mixture to several thousand degrees, followed by rapid cooling. While the gas is at a high temperature it reaches a state of near, or complete, thermodynamic equilibrium, during which many molecules, radicals and atoms are stable and are present in relatively large concentrations. Amino acids, however, are not stable at these temperatures. During the rapid cooling, the species present at high temperatures recombine, presumably via a chain mechanism, to form relatively complex organic molecules, such as amino acids and, if the cooling rate is sufficiently large, not enough high energy molecular collisions occur to break-up these complex molecules. Slow cooling would have resulted in a composition which does not contain any appreciable concentration of amino acids or their building blocks. The shock synthesis bypasses two obstacles: the instability of amino acids at high temperatures and the low concentration of their building blocks at low temperatures. This is the qualitative explanation for the high efficiency observed experimentally (Bar-Nun *et al.*, 1970).

Shock waves associated with large meteorites and thunder have been suggested as energy sources for the production of amino acids by Hochstim (1963) and Bar-Nun *et al.* (1970). The latter is especially attractive because of its abundance. (We have used the term 'thunder' for convenience and to distinguish it from the lightning leader. However, the time period of interest here is that in which the shock is strong and close to the source. Strictly speaking, thunder occurs considerably later and further away, when the shock wave has decayed to a sound wave.) Using the experimental efficiency of about 5×10^{10} molecules/erg and the present day frequency and power of thunder, it was hypothesized by Bar-Nun *et al.* (1970) that this process might have been a major source of amino acids in pre-biological times. However, it remained to be shown that thunder meets the two essential requirements for successful synthesis of amino acids, i.e., high initial temperature and rapid quenching. The purpose of this note is to report the results of an approximate study of the gas dynamics of thunder and some of the accompanying chemical changes in an assumed primordial atmosphere.

The composition of the atmosphere influences the propagation rate (shock speed) and the associated thermodynamic behavior of the thunder. In order to compare the present results with those of the experiment (Bar-Nun *et al.*, 1970) a mixture of 72% methane, 25% ammonia and 3% water (by volume) was used, realizing that the composition of the primordial atmosphere is subject to considerable uncertainty.*

In the familiar process of lightning, the sudden release of electrical energy greatly raises the temperature and pressure in a narrow region of atmospheric gas along the path of the stroke (the leader). The hot, high pressure gas expands outward from the core and, in a very short time, forms at its front a supersonic blast wave, i.e., a sharp wave front across which pressure, temperature and density rise discontinuously. For present calculational purposes, the lightning-produced shock wave phenomena can be adequately approximated by the so-called cylindrical 'blast wave theory' (Lin, 1954) for a single lightning stroke. The 'theory' is based on the assumption that most of the lightning energy (that part which is not radiated away by the incandescent gas) is concentrated in an infinitesimally slender cylindrical column and is discharged instantaneously into the gas. Nevertheless, chemical and thermodynamic equilibrium are assumed to exist at all times, although this assumption may be invalid for a short period (on the order of 0.1 to 1 μsec) immediately after the lightning.

Using a rough average of values mentioned by Jones *et al.* (1968) and Krider *et al.* (1968), it was assumed that an energy of 2×10^5 J/m is transferred to the gas, and assuming an initial atmospheric pressure of one atmosphere, one obtains the shock velocities and distances from the core of the column shown in Figure 1A as functions of time. Note that about 1 μs after the lightning discharge, the shock wave is 2 cm from the core and has a velocity of 10 km/s; at 60 μs, the shock has moved to 15 cm and is travelling at only 1.25 km/s. Simultaneously, the temperature of the gas compressed by passage of the shock wave drops by about 5000 K, immediately behind

* McGovern (1969) suggests that a primary atmosphere of methane, 10–15% hydrogen, and some ammonia and water vapor existed for about 0.5 to 1×10^9 yr, eventually changing to one consisting mainly of free nitrogen, carbon dioxide, carbon monoxide and water vapor. In the primary atmosphere, nitrogen was present only in the form of ammonia and probably in very small concentrations, since most of it was dissolved in the oceans; in the secondary, oxidized, atmosphere, amino acids cannot be produced (Miller and Urey, 1959). However, during an intermediate period of about 10^8 yr, the hydrogen mole fraction may have been only 10^{-4} (McGovern, 1969), in which case free nitrogen could coexist with methane (Urey, 1968). For amino acids production, an atmosphere with sizeable concentrations of free nitrogen is more favorable than one containing small amounts of ammonia for an order of magnitude longer time. Hence, it is possible that most of the nitrogen containing compounds were produced during this relatively short period.

the shock (see dashed line, Figure 1B). This rapid deceleration of the shock wave and accompanying cooling of the hot compressed gas behind the shock is the result of a constant amount of energy being distributed into a fast growing (as the square of the

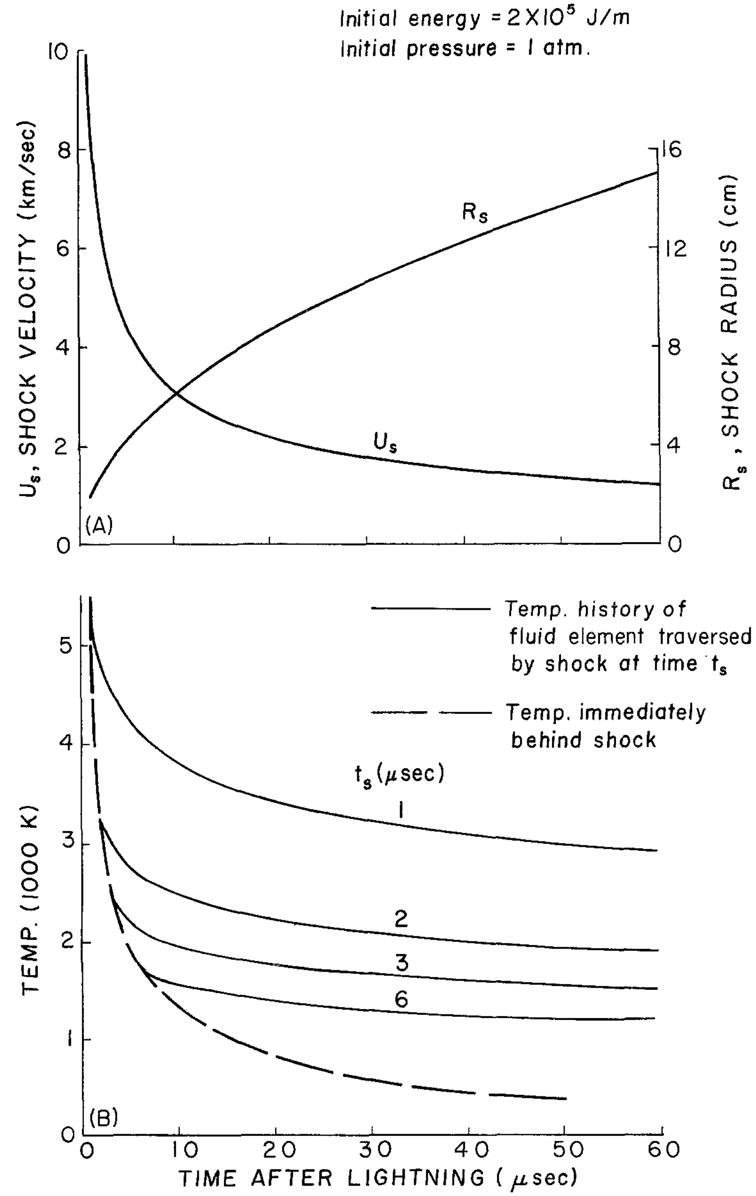

Fig. 1. Approximate gas-dynamical behavior of a lightning-produced shock wave: (A) Variation of shock wave velocity and radius with time; (B) Temperature histories immediately behing shock wave and of four elements of fluid.

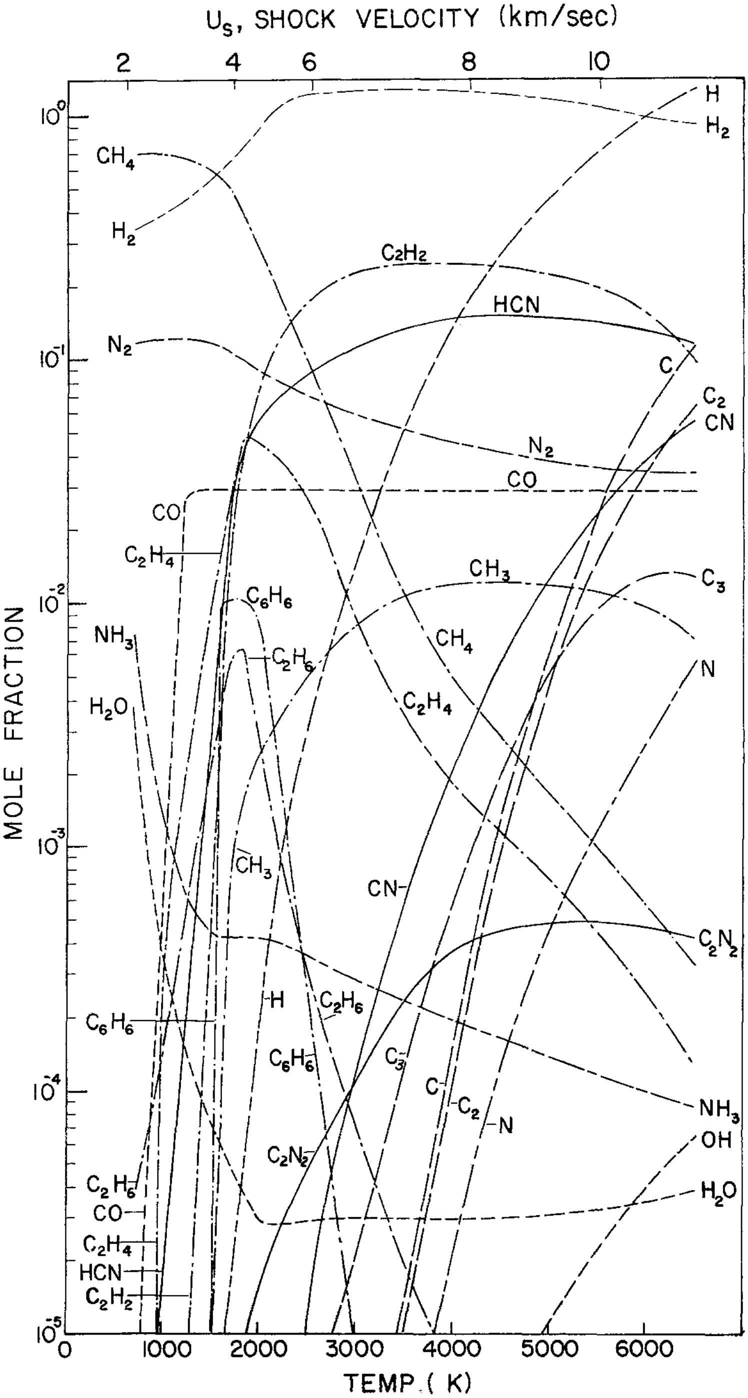

Fig. 2. Equilibrium species concentrations as functions of temperature.

shock radius) mass of atmospheric gas and, also, into changing the chemical composition of the compressed gas.

The equilibrium temperature and composition right behind the shock wave were computed with the aid of a shock program from Cornell Aeronautical Laboratory (Williams and Garr, 1966), using the shock speeds of Figure 1A. Not all species stable at these temperatures could be taken into account in the computation and the results presented in Figure 2 are indicative only of the relative concentrations of each group of compounds. Note that a major constituent of the high temperature gas is HCN which has been shown to be a precursor of amino acids (Miller, 1955). Around 2000 K, relatively large amounts of two-carbon and six-carbon species are present, enabling the formation of more complex amino acids. During equilibrium, the composition of the gas mixture is determined by the temperature, pressure, the initial atom ratio, and the thermodynamic properties of the product species only. The initial composition determines only the temperature which will result from a given shock speed. Only a small variation occurs when we substitute methane, or other low molecular weight hydrocarbons, for the ethane used in the experiment of Bar-Nun *et al.* (1970).

The exact mechanism of amino-acid production during quenching is still speculative and under investigation. However, in the shock tube experiment (Bar-Nun *et al.*, 1970) performed with an atom ratio mixture nearly identical to that assumed here, 36% of the ammonia was converted to the amino acids glycine, alanine, valine and leucine.

To determine whether thunder meets the requirements for efficient production of amino acids (i.e. quick heating followed by rapid cooling), we have computed the cooling rates of four elements of fluid after passage of the shock wave, using the work of Chernyi (1961) and Oppenheim *et al.* (1970) as an aid. Figure 1B contains the approximate temperature histories of these four elements (solid lines). The element of fluid closest to the lightning column (2 cm away) is traversed by the shock 1 μs after the lightning discharge and the subsequent temperature history is given by the line labeled $t_s = 1$. Similarly, temperature histories are shown for those elements traversed by the shock after 2, 3 and 6 μs and located initially at distances of 2.8, 3.4 and 4.8 cm, respectively, from the core. While the cooling rates are greatest right after the passage of the shock, and decrease thereafter, the average values over most of the temperature range of interest vary from about 0.5 to 5×10^7 K/s. These cooling rates exceed the experimental rates of Bar-Nun *et al.* (1970) by an order of magnitude. However, this is to be expected from a comparison of the geometry of the two cases; the expansion of the blast wave, which is a two-dimensional process, dissipates energy more quickly than the shock tube flow which is constrained to one dimension. Furthermore, there is no reason to believe that the quicker cooling of the blast wave would result in a lower amino acid production efficiency than that of the shock tube flow. It is only essential that the rates are not significantly *less* than those of the experiment.

Bar-Nun *et al.* (1970) estimated the thunder energy rate, per unit surface area, as 1 cal/cm^2/yr. Applying the results of the present calculation to this energy rate leads to a value of about 0.4 cal/cm^2/yr of energy directly available for amino acid production. Thus credence is lent to the speculation that lightning-produced shock waves may have been a major energy source in the production of organic molecules which, eventually, led to the emergence of life.

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