ELECTRICAL ENERGY SOURCES FOR ORGANIC SYNTHESIS ON THE EARLY EARTH

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Abstract. In 1959, Miller and Urey (*Science* **130**, 245) published their classic compilation of energy sources for indigenous prebiotic organic synthesis on the early Earth. Much contemporary origins of life research continues to employ their original estimates for terrestrial energy dissipation by lightning and coronal discharges, 2×10^{19} J yr^{-1} and 6×10^{19} J yr^{-1}, respectively. However, more recent work in terrestrial lightning and point discharge research suggests that these values are overestimates by factors of about 20 and 120, respectively. Calculated concentrations of amino acids (or other prebiotic organic products) in the early terrestrial oceans due to electrical discharge sources may therefore have been equally overestimated. A review of efficiencies for those experiments that provide good analogues to naturally-occurring lightning and coronal discharges suggests that lightning energy yields for organic synthesis (nmole J^{-1}) are about one order of magnitude higher than those for coronal discharge. Therefore organic production by lightning may be expected to have dominated that due to coronae on early Earth. Limited data available for production of nitric oxide in clouds suggests that coronal emission within clouds, a source of energy heretofore too uncertain to be included in the total coronal energy inventory, is insufficient to change this conclusion. Our recommended valves for lightning and coronal discharge dissipation rates on the early Earth are, respectively, 1×10^{18} J yr^{-1} and 5×10^{17} J yr^{-1}.

1. Introduction

The comparative importance of various energy sources for the production of prebiotic organic molecules on early Earth was first assessed by Miller and Urey (1959). While these authors identified solar ultraviolet light (UV) as the most abundant energy source contributing to organic synthesis in a reducing atmosphere, they also noted that electrical discharge sources (lightning and coronae) were second to UV in total power (energy per unit time averaged over Earth's surface), and would act closer to the surface, leading to more efficient transfer of products to the oceans. Recent work for 'neutral' oxidation state, largely carbon dioxide atmospheres, now generally viewed as more likely candidates for the atmosphere of early Earth (Walker, 1986), has suggested that organic synthesis due to electrical discharge would have been comparable in importance to any other terrestrial source (Stribling and Miller, 1987). These estimates have helped to reassure experimenters of the relevance of electrical discharges (convenient laboratory energy sources) to terrestrial prebiological organic chemistry. However, such calculations are based upon Miller and Urey's original estimates of global lightning and coronal sources of energy, now over thirty years old. Although their values remain those typically cited in the origins of life literature (Bar-Nun *et al.*, 1970; Fox and Dose, 1972; Miller and Orgel, 1974; Miller *et al.*, 1976; Day, 1984; Stribling and Miller, 1987; Oró *et al.*, 1990), and in biology textbooks (e.g., Dose, 1972; Darnell *et al.*, 1990;

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Strickberger, 1990), more recent work in terrestrial lightning and point discharge research suggests that they are overestimates by factors of about 20 and 120, respectively. Calculated concentrations of amino acids (or other prebiological organic products) in the early terrestrial oceans due to electrical discharge sources may therefore have been equally overestimated.

To our knowledge, all attempts to estimate electrical sources of energy available for early terrestrial organic synthesis have assumed that lightning and coronal energy discharge rates on early Earth were the same as those today. While we examine this assumption more carefully below, there appears to be no better way to attack the problem, and we adopt it here. We note, however, that this assumption could be the dominant source of uncertainty in our conclusions.

2. Lightning Discharges

Before proceeding to quantitative estimates, we briefly review terminology from lightning research (detailed presentations may be found in Schonland, 1953; Chalmers, 1967; Uman, 1969; Dawson, 1980, and Uman and Krider, 1989). Lightning can take place entirely within a cloud (intracloud discharges), between a cloud and the earth (cloud-to-ground discharges), between two clouds (cloud-to-cloud discharges), or between a cloud and the surrounding air (air discharges). The latter two types of discharge are comparatively rare. Although intracloud discharges are more common than cloud-to-ground discharges, cloud-to-ground discharges are by far the better studied of the two. (Differences in frequency and discharge energies between the two will be further discussed below.) A typical cloud-to-ground discharge develops roughly as follows (Uman, 1969; Dawson, 1980; Uman and Krider, 1989): As a result of poorly-understood processes of charge separation in a thundercloud, local electrical breakdown occurs, mobilizing electric charges that were previously attached to ice and water particles. The resulting negative charge concentration at the cloud base initiates a negatively charged column, the 'leader', which then propagates downward. For reasons that remain unclear, this initial leader grows towards the ground in a stepwise fashion. Once sufficiently close to the ground, the high negative potential results in an electric field sufficient to cause upward-moving discharges to be launched from the ground to the leader tip. The leader than acts as a transmission line, emptying its charge to ground, first from its tip, and then from successively more distant points. This creates the 'return stroke', a wave of luminosity moving from ground to cloud. Most of the energy of the discharge is released in this first stroke. The first stroke is often followed by successive leader/return-stroke sequences (successive leaders are termed 'dart leaders', and travel in a smooth, rather than stepwise, pattern), along the original channel, at intervals of ~40 msec. This complete sequence, which appears to the eye as a flickering, jagged chain, typically extends for ~0.2 sec, only a little longer than the time-resolution limit of human vision, and is termed the flash.

Miller and Urey (1959) based their estimates of global energy dissipation from

TABLE I

Estimates[a] of lightning flash discharge energy (J flash^{-1})

Reference	Energy
Schonland (1953)	6×10^9
Hill *et al.* (1980)	8×10^7
Borucki and Chameides (1984)	4×10^8

[a] See text for discussion of uncertainties.

lightning and coronal discharges on the best data available in 1959, those summarized by Schonland (1953). Schonland (his Sections 30,31) cited estimates that about 100 flashes of lightning occur over the surface of the Earth each second. (Of these, he took 1 in 4 to be a cloud-to-ground discharge. Schonland made no distinction between cloud-to-ground and intracloud flashes in his estimates of energy dissipation.) He then reviewed (his Section 34) estimates of current discharges and potential differences in typical flashes. With a choice for a typical lightning flash discharge energy of 6×10^9 J, Schonland's results yield 2×10^{19} J yr^{-1} of electrical energy from terrestrial lightning, which is the value given by Miller and Urey.

The largest source of error in this result comes from an overestimate of the energy dissipated per lightning flash. Various estimates for this value are summarized in Table I. Both Hill *et al.* (1980) and Borucki and Chameides (1984) based their values on extensive reviews of measurements of the energy dissipated in cloud-to-ground return strokes.

Hill *et al.* (1980) calculated terrestrial annual energy dissipation by lightning using a review by Hill (1979a), who examined four independent methods of estimating the energy dissipated along a cloud-to-ground first return stroke. One of these methods, acoustical measurements, yielded numerical values ranging over three orders of magnitude (10^2 to 10^5 J m^{-1}). Two others, electrical and theoretical estimates, ranged from 5×10^3 to 8×10^4 J m^{-1}, and from 3×10^3 to 2×10^4 J m^{-1}, respectively. [A more recent theoretical estimate of lightning energy dissipation gave a value $\sim 4 \times 10^3$ J m^{-1} (Paxton *et al.*, 1986), smaller by a factor ~2.5 than that preferred by Hill (1979a); this result remains controversial, however (Hill, 1987)]. The sole determination of electrical energy dissipation per unit length by an optical method gave a result of 2×10^5 J m^{-1}; Hill (1979a) argued that this value should be revised downward by a factor of ~ 20. Hill (1979a) and Hill *et al.* (1980) gave a preferred value for the electrical, optical, and theoretical estimates of $\sim 10^4$ J m^{-1}. [Note that optical measurements of lightning return strokes indicate that stroke luminosity, and therefore probably energy dissipation, decays with height (Guo and Krider, 1982). All estimates of lightning energy dissipation per unit length must therefore be understood to represent average values only]. Hill (1979a) gave the range of lengths for lightning strokes as 1 to 12 km, in agreement with other authors [for example, Uman (1969) gives a typical range to be 2 to 12 km]. The upper value is roughly the thickness of the troposphere. Hill *et al.* (1980) chose 5 km as an average value, again a typical selection (Uman, 1969). This gives the total energy dissipated by a first stroke along its length to be 5×10^7 J.

The number of strokes in an individual lightning flash has been observed to range from 1 to 26 (Uman, 1969). Some 20% of flashes appear to be single strokes (Hill, 1979a). Estimates in the literature for the averate number of strokes per flash vary from 3 to 5 (Uman, 1969; Berger, 1977; Chameides *et al.*, 1977; Hill, 1979a; Hill *et al.*, 1980; Borucki and Chameides, 1984). However, subsequent strokes are typically less energetic than the first (Hill, 1979a; Hill *et al.*, 1980, Dawson, 1980; Borucki and Chameides, 1984). Dawson (1980) has argued that for this reason, the best approximation for molecular synthesis calculations is simply to count only the first stroke. Other authors, however, have incorporated the energy discharged in subsequent strokes. Hill *et al.* (1980), for example, used measurements of the charge transferred by the first and subsequent strokes, to conclude that the ratio of energies of successive strokes is approximately 2:1. Taking a three-stroke flash as typical, they concluded that a typical flash dissipates 1.5 ± 0.5 times as much energy as the first return stroke alone, giving about 8×10^7 J dissipated per flash.

What is the frequency of lightning flashes over the Earth? The modern estimate (Hill *et al.*, 1980; Borucki and Chameides, 1984) for the global flash rate, 100 $\sec^{-1}$, remains the same as the historical value (Schonland, 1953). Satellite observations of nighttime thunderstorms from the OSO-B satellite, reported in 1970 by Vorpahl *et al.*, suggested a global nighttime average of ~30 $\sec^{-1}$; however, these authors noted that some nighttime flashes may have been missed due to a combination of cloud cover and threshold limits. More recent results from the Defense Meteorological Satellite Program confirm the historical value. Orville and Spencer (1979) found a global frequency of 96 flashes flashes s^{-1} for dusk observations, and 123 flashes s^{-1} for observations made at midnight. Turman and Edgar (1982) found 80 ± 40 flashes s^{-1}, with 10% variation through the seasons. From an entirely different direction, Prentice (1977, Sec 2.3.2) reviewed results from visual, flash counter, and power transmission-line performance studies of cloud-to-ground flash frequencies; rates were observed to vary from 0.2 to 12.1 flashes km^{-2} yr^{-1}, bracketing the historical observations cited by Chalmers (1967, Section 14.34). Extrapolating these results globally, while incorporating the observation (Vorpahl *et al.*, 1970) that 10 times as many lightning flashes occur over land areas as over the sea (~70% of Earth's surface area), yields a flash frequency of 1.2 to 71 cloud-to-ground flashes s^{-1}. In temperate climates, the frequency of intracloud flashes is ~3, and in tropical climates, ~6, times that of cloud-to-ground flashes, respectively (Prentice, 1977). This observed latitudinal variation (Chalmers, 1967; Prentice, 1977) yields a globally averaged intracloud/cloud-to-ground flash ratio of ~4 (Chameides *et al.*, 1977). Scaling the observed cloud-to-ground flash frequency by this factor yields (very) rough agreement with the satellite observations, which are clearly the more reliable. It is unclear how the value of 100 flashes s^{-1} would have differed on an early Earth which may have had very little continental mass, and a possible dense CO_2

atmosphere (Walker, 1986).

With 100 flashes s^{-1}, and an average energy of 8×10^7 J per flash, Hill *et al.*'s (1980) values yield a global lightning energy dissipation rate of 2×10^{17} J yr^{-1}, a value some 100 times below that suggested by Miller and Urey. (Results are summarized in Table II).

However, Borucki and Chameides (1984) have recently reviewed optical and electrical measurements of lightning energy dissipation, supplementing the measurements cited by Hill (1979a) with additional data, while excluding some of the more extreme determinations. Moreover, these authors employ the results of field measurements that give the total energy dissipated by the entire first return stroke, rather than an energy dissipation per unit length. Therefore, estimates of the length of the discharge column need not be made. In fact, for measurements of lightning energy dissipation, only rarely are estimates of the height of the discharge available. For this reason, Borucki and Chameides (1984) are able to average over many more optical and electrical measurements than is Hill (1979a). Borucki and Chameides choose 4 strokes per flash as typical, and argue that subsequent strokes dissipate about one quarter as much energy as the first return stroke. They thereby find an average energy dissipation for optical and electrical measurements of 4×10^8 J per flash with an uncertainty of a factor of 2.5. Choosing a global frequency of 100 flashes s^{-1}, they find a global energy dissipation rate of 1×10^{18} J yr^{-1}, a factor 5 greater than that of Hill *et al.* (1980), and a factor of 20 smaller than that found by Miller and Urey (1959).

Hill's (1979a) estimate for energy dissipation by a typical return stroke was given only to a certainty of 'on the order of' 10^8 J m^{-1}, leading to an estimate of lightning flash discharge energy $\sim 8 \times 10^7$ J per flash. We adopt in this paper the more recently determined value (4×10^8 J per flash) preferred by Borucki and Chameides (1984), recalling that this value is uncertain to a large factor ($\sim$3). The lower end of the Borucki and Chameides error bar overlaps the uncertainties in the value preferred by Hill (1979a) and Hill *et al.* (1980). Similar considerations obviously also hold for these authors' estimates of the global energy dissipation rate.

TABLE II

Estimates[a] of electrical energy available for organic synthesis on early earth (J yr^{-1})

Reference	Lightning	Coronal discharge
Miller and Urey (1959)	2×10^{19}	6×10^{19}
Hill *et al.* (1980)	2×10^{17}	–
Chameides and Walker (1981)	2×10^{18}	–
Borucki and Chameides (1984)	1×10^{18}	–
This work	1×10^{18}	5×10^{17}

[a] See text for discussion of uncertainties.

The energy of an individual lightning flash is partitioned primarily into ohmic dissipation and shock-wave passage (thunder). An important uncertainty is the relative importance of these two mechanisms, as calculations of prebiotic organic production rely on extrapolations from experimental efficiencies derived from simulating one or the other process. Dawson (1980) argues that nearly instantaneous energy release would be well-modeled by ideal shock heating, whereas in a slower and more diffuse release, ohmic heating would be the more important dissipation mechanism. Real lightning evidently lies between these two extremes; Dawson (1980) holds that intracloud strokes are poorly modeled by an instantaneous release model, as they differ from cloud-to-ground strokes in that they generate only weak return strokes (see also Uman and Krider, 1989). Hill (1979b) has argued that no more than ~10% of lightning energy dissipation goes into shock heating. Even if we were to assume 100% efficiency in converting the energy discharge of all strokes into shocks, previous estimates (Bar-Nun *et al.*, 1970; Miller *et al.*, 1976; Oró *et al.*, 1990) that 2×10^{19} J yr^{-1} were available for shock processing by thunder on the early Earth must be revised. Moreover, these researchers' conclusion that shock waves from lightning were more important by a factor of 10 than were atmospheric shocks from asteroid and comet impacts during the heavy bombardment of early Earth no longer stands. Rather, the relative importance of the two sources for terrestrial atmospheric shocks now appears to have been roughly comparable (Chyba and Sagan, 1991).

Chameides and Walker (1981) employed an average rate of dissipation of energy by lightning for the early Earth of $\sim 2 \times 10^{18}$ J yr^{-1}, a value ~3 times greater than that we advocate here. Unfortunately, these authors did not present the calculations leading them to this value, but we have included it in Table II for completeness. An earlier calculation by Chameides *et al.* (1977) yielded 3×10^{19} J yr^{-1}, a value higher than Miller and Urey's (1959) result. However, Chameides *et al.*'s (1977) choice for energy dissipation in a single lightning flash (2×10^9 J per flash), as well as their argument for a global flash rate of 400 flashes s^{-1}, are now agreed to have been in error (Dawson, 1980; Borucki and Chameides, 1984), so we have not included these estimates in Tables I and II.

Finally, we note that an alternative approach to calculating global lightning energy dissipation on the early Earth would by analogy to Borucki *et al.*'s (1984) attempt to estimate the lightning dissipation rate, E_L, on the saturnian moon Titan. These authors calculated E_L via the equation $E_L = RE_C$, where R, the ratio of Titan's lightning energy-dissipation rate to its convective energy rate, was taken to lie between that of Earth and Jupiter. E_C, the convective energy rate, depends linearly on both the solar flux, and the fraction of that flux, f, which reaches the layer of the atmosphere in which lightning occurs. Unfortunately, trying to estimate the lightning discharge rate for the early Earth through this method seems to provide no advantages over simply setting the rate for early Earth equal to that of today. R must be taken from the contemporary Earth, so E_L will differ from a direct extrapolation from lightning discharge rates on the present-day Earth only if E_C differs. E_C, however, is proportional to f (which for the early Earth can only be guessed at), and to the solar flux. While it is true that the early Sun would have been less luminous than the Sun of today (cf. Sagan and Mullen, 1972), the magnitude of this difference was $\lesssim 30\%$ (see, for example, Zahnle and Walker, 1982) around the time of interest for the origins of life, $\sim$ 4 Gyr ago. This difference is small compared with the uncertainties in the problem.

3. Coronal Discharges

Miller and Urey (1959), again relying on Schonland (1953), estimated that coronal discharge was a more important source of electrical energy for organic synthesis than lightning by a factor of ~ 3. How does their estimate of 6×10^{19} J yr^{-1} fare in light of more recent research into terrestrial point discharges? To answer this question, we first review the physical nature of such discharges, discuss Schonland's results, and summarize subsequent critiques of his work. We conclude with a new estimate, based on recent data.

Historically, there was agreement in the atmospheric electricity literature that coronal discharges from pointed objects were the dominant mechanism for transfer of charge between thunder clouds and the Earth (Schonland, 1928, 1953; Chalmers, 1951, 1967; Stromberg, 1971). Such discharges are also often called point discharges. (See Section 4 below for a review and clarification of the variety of terminology used in electrical discharge research.) The mechanism of point discharge is well-understood (Schonland, 1953; Chalmers, 1967; Latham and Stromberg, 1977); the tip of any sharp object will act to concentrate a local electric field, causing breakdown and an electron avalanche (coronal discharge) for sufficiently high field values. 'Sharp' in this context may mean objects as seemingly 'blunt' as water droplets or wave crests, provided electric fields of sufficient magnitude are present (Latham, 1975; Toland and Vonnegut, 1977; Latham and Stromberg, 1977), a complication discussed further below. Nevertheless, it is thought that by virtue of their relative height, pointed geometry, and large numbers, trees may be the main terrestrial objects for which point discharge occurs today (Schonland, 1953; Chalmers, 1967; Stromberg, 1971; Ette and Utah, 1973).

Schonland's (1953) quantitative treatment of point discharge was based on his pioneering earlier work in South Africa (Schonland, 1928). In these studies, Schonland took an actual tree, supported it on insulators, and connected it to the Earth through a galvanometer. Once the tree withered, fresh twigs and leafy branches were occasionally wired to it. Schonland then measured currents through the tree during thunderstorms, when electric field strengths were high enough to cause point discharge. By estimating the average spacing of live trees beneath the storm, Schonland extrapolated his measurement for a single tree to an estimate of an upward point discharge current density 3.3×10^{-8} A m^{-2} beneath a typical thunderstorm, or 2.1 A beneath an estimated effective storm radius of 4.5 km. (In the SI system of units, one ampere (A) is defined as the flow of one coulomb

(C) of charge per second). Multiplication of this current by the potential below the thundercloud prior to discharge yields the total energy dissipated by point discharge beneath the storm. Schonland (1953, Section 34) considered simple spherical cloud models, and calculated the maximum potential reached prior to discharge for different estimates of thundercloud electric fields. His first model suggested potentials of around 4.2×10^8 V, with subsequent estimates varying by factors of 1/3 to 10 about this value. The choice 4.2×10^8 V gives a value for energy dissipation in a thunderstorm due to point discharge of $(4.2 \times 10^8 \text{ V})(2.1 \text{ A}) \approx 9 \times 10^5$ kW, about 3 times higher than Schonland's estimate of 3×10^5 kW dissipated by lightning discharges in the storm. As noted above, Miller and Urey (1959) gave a global coronal energy discharge rate ~3 times greater than that due to lightning.

It is only to be expected that Schonland's measurements have been criticized and improved upon in the 60 yr subsequent to his initial work. Chalmers (1967, Section 9.8) noted that the tree Schonland employed in his experiments was not in natural surroundings, and that the trees nearest to it were considerably more distant than the average 5 m separation that Schonland assumed. Chalmers suggested that Schonland's experiment may therefore have overestimated average currents, perhaps by a factor ~4. Over the past 30 yr, considerable progress has been made in the ability of experiments to accurately measure point discharge currents from living trees – an important improvement as the sap of a living tree may be its most important conductor of electricity [see Latham and Stromberg (1977) for a review]. Moore and Vonnegut (1977) conducted experiments with a small forest of potted trees under thunderstorms, and found current densities 'of up to' 10^{-8} A m^{-2}, a maximum value several times smaller than Schonland's result. The best recent measurements give an average value an order of magnitude smaller. Careful measurements on a living spruce tree plantation (Stromberg, 1971) found a net charge transferred through a tree on the inside of the plantation of -156 μC in 31 min, giving a current density 2.3×10^{-9} A m^{-2} for an average tree spacing of 6 m (Stromberg, 1971; Ette and Utah, 1973; Latham and Stromberg, 1977). Extensive measurements (Ette and Utah, 1973) with palm trees, metal points, and grass yield mean discharge current densities of $(1.2 \pm 0.2) \times 10^{-9}$ A m^{-2}, in approximate agreement with the spruce plantation result. Choosing a typical effective storm cloud area to be 50 km^2 (Ette and Utah, 1973; Latham and Stromberg, 1977) then gives total currents of 0.12 and 0.06 A for the two sets of results [note that Latham and Stromberg (1977, p. 107) list the latter value incorrectly as 0.6 A, an error that has unfortunately been propagated in the literature (e.g., Hill *et al.*, 1984, Sec. 5.2)]; we therefore take 0.09 A as a mean contemporary estimate for the current that flows beneath a typical thunderstorm. This value is ~20 times smaller than that found by Schonland.

An objection to the use of such contemporary thunderstorm point discharge measurements for calculations pertaining to early Earth is the obvious one that no trees, or any of the other pointed objects used in the measurements cited, existed prior to the origins of life. This objection may not be as important as it initially appears, however, due to the theoretical argument (Chalmers, 1951; Moore and Vonnegut, 1977) that the total point discharge current below a cloud is nearly independent of the nature of the points beneath it. Electric field intensity over 'blunt' surfaces will simply build to the threshold level necessary for discharge from these surfaces (Toland and Vonnegut, 1977). This argument receives support from observations that electric field intensities over water during storms reach values as high as 130 kV m^{-1}, a factor ~10 higher than those needed for discharges from trees and metal points (Stromberg, 1971; Moore and Vonnegut, 1977), and in good agreement with laboratory determinations of the field strengths (~200 kV m^{-1}) necessary to produce coronal discharges in splashes, water droplet collisions, and bubble bursts (Latham, 1975; Latham and Stromberg, 1977).

What, then, is the energy dissipated by point discharge by an average thunderstorm on contemporary Earth? This calculation requires knowing the potential difference between the thundercloud and ground. Uman (1969) estimates a typical potential difference of 1×10^8 V, which lies at the lower end of the range given by Schonland. Moore and Vonnegut (1977) give electric field strengths below thunderstorms ranging from 10^4 V m^{-1} over land to 10^5 V m^{-1} over oceans, bracketing Uman's (1969) value, for a cloud-ground separation of 5 km. Toland and Vonnegut (1977) list seven measurements of electric fields at lake surfaces during thunderstorms; their value of $(6\pm4) \times 10^4$ V m^{-1} corresponds to a potential of $(3\pm2) \times 10^8$ V for a 5 km separation. As ~90 % of lightning flashes occur over land (Vorpahl *et al.*, 1970), we choose 1×10^8 V for our calculations, with an uncertainty given by the ranges cited above of a factor ~5. Then, given a typical point discharge current of 0.09 A beneath a thundercloud, we find 9×10^3 kW energy dissipated by coronal discharge. How does this compare with the energy dissipated by lightning for a typical storm? Prentice (1977, Section 2.3.3) has reviewed recent measurements of flash rates during storms; a good global average value appears to be 3 flashes min^{-1}, in excellent agreement with historical estimates (Schonland, 1953). Taking an average flash to dissipate 4×10^8 J, a typical storm dissipates energy by lightning at a rate 2×10^4 kW, so that energy dissipation by coronal discharge is roughly comparable to that of lightning. The global coronal discharge energy rate is then approximately 5×10^{17} J yr^{-1} (with a factor ~5 uncertainty), or 120 times less than the original estimate of Miller and Urey (1959).

4. Electrical Discharge Terminology: Hot and Cold Plasmas

Before proceeding to a discussion of energy yields for organic synthesis of laboratory simulations of lightning and coronal discharges, we first review electrical discharge terminology. Different laboratory simulations provide reasonable analogues to either lightning or coronal discharges, whereas some do not appear to provide unambiguous representations of either naturally-occurring energy source. Some clarification of the terminology used to describe, and the basic physics of, different electrical discharge sources used in the laboratory therefore seems necessary.

Laboratory discharges depend upon creating a potential between a cathode and anode that is sufficiently high to achieve the breakdown voltage of the background gas. Upon breakdown, the gas is transformed from an insulator to a conductor. Penning (1957) and Bell (1967) have reviewed the variety of ways this transformation may take place. For parallel flat plate electrodes in ordinary air at atmospheric pressure, as soon as the breakdown voltage is reached, a current of high intensity and short duration (that is, a spark) will occur. At lower gas pressures, however, a self-sustaining 'glow discharge' may be produced, in which the cathode continuously emits electrons due to ion bombardment. Typical currents in laboratory glow discharges are in the range 10^{-2} - 10^{2} mA. Thermal effects are negligible and not necessary for sustaining the discharge. At higher currents, however, the cathode temperature rises rapidly, and the cathode gives off electrons by thermionic emission. This form of discharge is therefore known as a thermionic arc, or simply as an arc discharge. Typical currents are above $\sim$0.1 A.

Glow discharges create 'cold plasmas', in which the electrons are highly superthermal, but the ions, neutral molecules, and molecular fragments in the background gas remain near the ambient temperature. What we have previously referred to as 'point discharges' are the natural-world analogues of laboratory glow discharges, but which occur at atmospheric pressure. As Darrow (1932) has explained, sparking may be avoided (and glow discharges produced) at atmospheric pressure, provided that one or both of the experimental electrodes is sufficiently curved. In practice, at least one of the electrodes must have a radius of curvature smaller than the distance between the two electrodes.

Historically, the appellation 'coronal discharge' has been used by some authors to mean a glow discharge in the case where the sharply-curved electrode was a wire (Darrow, 1932; McTaggart, 1967). However, Chalmers (1967, p. 239) defined 'coronal discharge' to mean any point discharge 'when investigated in the laboratory'. At least as early as Darrow (1932), however, 'coronal discharge' was sometimes also being used as a simple synonym for 'glow discharge'. In a similar inconsistent usage, the name 'point discharge' has not always referred exclusively to discharges outside the laboratory: McTaggart (1967) used this term to denote a specific experimental geometrical configuration, *viz.* one where at least one electrode was a point, or at least sharply curved. Because of these various conflicting usages, we must define our own convention. We take 'coronal discharge' to be synonymous with 'glow discharge', whether in the natural world or laboratory; no specific electrode geometry is connoted. We take 'point discharge' to have a more restricted meaning, *viz.* a coronal discharge where one or both (natural or laboratory) electrodes has a high radius of curvature.

The common physical characteristic of all these discharges is that each creates a cold plasma. We may therefore expect other discharges that similarly create cold plasmas to provide adequate simulations of the chemical effects of naturally-occurring point discharges (see Section 5 below). Such laboratory discharges include radio-frequency cold plasma discharges induced by either capacitative or inductive coupling (Bell, 1967; Thompson *et al.*, 1991).

Arc discharges may also produce cold plasmas, provided that pressures and currents are sufficiently low (Brown, 1966; Bell, 1967). Sufficiently high current arcs, however, create 'hot plasmas', in which the kinetic and excitation temperatures of all species – electrons, ions, molecules, and molecular fragments – are very high (Bell, 1967; Thompson *et al.*, 1991). Arc discharges operating at pressures at or above one atmosphere typically create hot plasmas, although at sufficiently low currents, an appreciable difference between the electron temperature and that of the other species may still exist (Brown, 1966; Bell, 1967). In the natural world, lightning is a hot plasma process (Thompson *et al.*, 1991), so that sufficiently-high-pressure arc discharges may provide adequate simulations. Laser-induced hot plasmas will also provide good laboratory simulations of lightning (Borucki *et al.*, 1988; Scattergood *et al.*, 1989).

5. Relative Organic Production from Lightning and Coronal Discharges

As shown in Table II, our preferred estimates of electrical energy available for organic synthesis on the early Earth give comparable values for net energy dissipation by lightning discharges and coronal discharges. However, the physics of lightning and coronal discharges is quite distinct, and the efficiency of organic synthesis from the two energy sources appears to differ substantially. As just discussed, coronal discharges create cold plasmas of superthermal electrons, whereas high voltage, high current arcs such as lightning create hot plasmas, in which the kinetic and excitation temperatures of all species are very high. It would not be surprising if energy yields for molecular synthesis varied according to whether the plasmas were hot or cold, and in fact this is found to be the case experimentally: Hot plasmas appear to be much more efficient for organic synthesis than cold plasmas.

Thompson *et al.* (1991) have summarized recent work on the energy yields for organic synthesis (e.g., nmole product per joule of energy in the discharge) from a variety of laboratory discharges. For production of HCN in CH_4/N_2 atmospheres, they find energy yields from a variety of cold plasma experiments to lie typically in the range ~10–20 nmole J^{-1}. Spark discharge experiments by Stribling and Miller (1987) reported yields of ~10 nmole J^{-1}, in good agreement with cold plasma results from coronal discharges and inductively-coupled plasma discharges. The Stribling and Miller spark discharge experiments took place at a pressure of 267 mbar, a pressure sufficiently low so that we might expect the plasma created to have been a cold one. The fact that three different mechanisms for generating cold plasmas yielded synthesis efficiencies identical to within a small factor suggests that any laboratory-created cold plasma will provide a reasonable simulation of natural point discharges. It is true that a low efficiency, ~3 nmole J^{-1}, was found (Thompson *et al.*, 1991) for an inductively-coupled plasma at very low pressures (0.24 mbar). However, efficiencies of other experiments appear to be pressure-independent over the range 13 to 267 mbar.

Organic synthesis in hot plasmas, by contrast, appears to be more efficient by about one order of magnitude. HCN production by laser-induced hot plasmas ranges from 93 to 249 nmole J^{-1} (Scattergood *et al.*, 1989). A thermochemical-hydrodynamic model by Chameides and Walker (1981) of HCN production by lightning gives just over 10^{17} molecules J^{-1}, or ~200 nmole HCN J^{-1}, consistent with the experimental results.

Lying between these efficiencies for hot and cold plasmas are a set of high-voltage arc experiments at pressures of approximately one atmosphere (summarized in Thompson *et al.*, 1991), with efficiencies ranging from 47 to 78 nmole J^{-1}. It is possible that these efficiencies lie between the results for coronal discharges and lightning because these arcs create plasmas where the ion and molecular temperatures are almost, but not quite, as high as that of the electrons. One set of arc discharge experiments have sometimes yielded efficiencies comparable to those of laser-induced hot plasmas. In an extensive set of experiments by Briner *et al.* (1919, 1938), HCN production efficiencies were found to vary from 49 to 361 nmole J^{-1} in CH_4/N_2 atmospheres at atmospheric pressure. Analogous experiments at pressures ranging from 155 to 328 mbar gave yields in the range 49 to 426 nmole J^{-1}. Experimental yields appeared to depend strongly on the frequency of the arc discharge, with a maximum efficiency achieved at $\sim 10^7$ Hz (Briner *et al.*, 1938).

HCN production seems to be approximately one order of magnitude more efficient for hot plasma discharges than for cold plasmas. The discrepancies of efficiencies for C_2H_2 production are even more pronounced: Hot plasmas appear nearly two orders of magnitude more efficient for C_2H_2 production than cold plasmas (see Thompson *et al.*, 1991, Table III). These comparisons carry an evident implication for the relative importance of lightning versus coronal discharge on the early Earth: Although the total energy dissipation on the early Earth from both sources appears to have been about equal, production of HCN and C_2H_2 by lightning apparently would have considerably overshadowed that by coronal discharge, perhaps by nearly an order of magnitude.

However, there are a variety of sources of coronal discharge energy that are included neither in our estimate here, nor in the earlier estimate by Miller and Urey (1959). These include coronal emission from highly deformed or colliding raindrops, as well as from the surfaces of cloud ice crystals (Latham and Stromberg, 1977). In addition, typical lightning stroke channels are probably surrounded by a coronal region (Hill *et al.*, 1984; Bhetanabhotla *et al.*, 1985).

This latter source of coronal discharge energy appears to be negligible compared with the point discharge sources evaluated in Sec. 3. Hill *et al.* (1984; see also Bhetanabhotla *et al.*, 1985) calculate the energy dissipated in the coronal sheath of a lightning stroke, and find it to be only 3×10^{-4} to 5×10^{-3} of that dissipated in the stroke itself. Table II shows that coronal sheath energy dissipation can therefore equal no more than 10^{-2} of that dissipated in terrestrial point discharges.

Upper limits on the importance of intracloud coronae have been placed by direct airborne observation of enhanced nitric oxide (NO) levels in the anvils of two cumulonimbus clouds (Ridley *et al.*, 1987; Chameides *et al.*, 1987). In these daylight flights, no direct observations of lightning flashes were made, although secondary evidence (e.g., radio static) indicated some electrical activity. It remains uncertain whether synthesis of the observed NO was primarily due to lightning or coronal discharges within the cloud. However, observed NO production extrapolated from the two clouds yields a global production rate of nitrogen oxides from electrified clouds of 7×10^9 kg N yr^{-1}, with an uncertainty of a factor of 3. As pointed out by Chameides *et al.* (1987), this result is in good agreement with entirely independent estimates (via an approach analogous to that used in Sec. 2 above) of global production of NO from lightning alone, which yield a range $(0.8–8) \times 10^9$ kg yr^{-1} (Borucki and Chameides, 1984). This suggests that coronal production of NO within clouds cannot exceed that by lightning by more than a small factor.

Ridley *et al.* (1987) have proceeded along slightly different lines than Chameides *et al.* (1987), and found an upper limit of NO production by coronal discharge within the clouds by assuming that all observed NO is due to coronae. This approach yields a net NO production of ~20 kg N hr^{-1}. As these authors point out, this is approximately half the rate expected by assuming a lightning discharge frequency within the cloud of 1 min^{-1} (see Section 3 above, where it was argued that the best contemporary value is about 3 flashes min^{-1} in a storm), and the Borucki and Chameides (1984) estimate of NO yield per lightning flash. Once again, we find that NO production by coronal discharge appears to be at most comparable to that due to lightning. This is unsurprising, since laboratory yields for NO due to coronae have been found to be 23 ± 12 n mole J^{-1} (Hill *et al.*, 1988), a value considerably below that found for production by lightning, 149 ± 33 nmole J^{-1} (Borucki and Chameides, 1984). (In both absolute and relative terms, these values are similar to those found for HCN production.) On the basis of the very limited data base (two clouds) provided by the airborne observations cited here, it seems unlikely that coronal discharges within clouds could provide a source of organic molecules which outweighs that due to lightning.

However, the data base clearly needs to be broadened. Both with respect to coronal sources within clouds, and regarding better estimates of global energy dissipation by lightning and point discharges, the origins of life community needs assistance from those scientists specializing in atmospheric electricity. Nevertheless, it now apears that those lightning and coronal energy discharge rates currently employed in the origins of life literature need to be substantially reduced. A comparison with other (indigenous and exogenous) energy sources for prebiotic organic synthesis on the early Earth is made in a new compilation by the authors (Chyba and Sagan, 1991).

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