

# ENERGY YIELDS FOR HYDROGEN CYANIDE AND FORMALDEHYDE SYNTHESSES: THE HCN AND AMINO ACID CONCENTRATIONS IN THE PRIMITIVE OCEAN

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**Abstract.** Prebiotic electric discharge and ultraviolet light experiments are usually reported in terms of carbon yields and involve a large input of energy to maximize yields. Experiments using lower energy inputs are more realistic prebiotic models and give energy yields which can be used to estimate the relative importance of the different energy sources on the primitive earth.

Simulated prebiotic atmospheres containing either CH<sub>4</sub>, CO or CO<sub>2</sub> with N<sub>2</sub>, H<sub>2</sub>O and variable amounts of H<sub>2</sub> were subjected to the spark from a high frequency Tesla coil. The energy yields for the synthesis of HCN and H<sub>2</sub>CO were estimated. CH<sub>4</sub> mixtures give the highest yields of HCN while H<sub>2</sub>CO is most efficiently produced with the CO mixtures. These results are a model for atmospheric corona discharges, which are more abundant than lightning and different in character. Preliminary experiments using artificial lightning are also reported.

The energy yields from these experiments combined with the corona discharge available on the earth, allows a yearly production rate to be estimated. These are compared with other experiments and model calculations. From these production rates of HCN (e.g. 100 nmoles cm<sup>-2</sup> yr<sup>-1</sup>) and the experimental hydrolysis rates, the steady state concentration in the primitive ocean can be calculated (e.g., 4 × 10<sup>-6</sup> M at pH 8 and 0°). A steady state amino acid concentration of 3 × 10<sup>-4</sup> M is estimated from the HCN production rate and the rate of decomposition of the amino acids by passage through the submarine vents.

## 1. Introduction

One of the goals of origin of life studies is to determine the composition of the primitive atmosphere and the organic compounds that could have been present in the primitive oceans. Without some knowledge of the organic compounds available, it is difficult to conduct realistic experiments in the further polymerization steps and the organization of these polymers into the first living organisms.

The types of organic compounds which could have been available in the primitive oceans will be determined by understanding such factors as the composition of the atmosphere, the sources of energy available to activate these components, the further reactions which occur in the oceans, and the rate of decomposition of organic compounds in the ocean. The usual prebiotic synthesis experiment takes a mixture of gases and applies a source of energy for a long period of time to obtain the maximum yield of organic compounds. This would be a good representation of synthesis on the primitive earth if there were only a single kind of energy available and the synthesis of organic compounds were not limited by this energy. However, there were a number of sources of energy on the primitive earth, as has been previously discussed (Miller *et al.*, 1976), and prebiotic synthesis was probably limited by the total quanti-

ty of carbon available in the atmosphere rather than by the energy available from the various sources (Miller and Schlesinger, 1984).

There is considerable controversy over the composition of the primitive atmosphere. (Chang *et al.*, 1983; Holland, 1984; Levine, 1985; Lewis and Prinn, 1984; Walker, 1977). Previous experiments in this laboratory have examined yields of amino acids (Schlesinger and Miller, 1983a) as well as hydrogen cyanide, formaldehyde, and ammonia (Schlesinger and Miller, 1983b) from various mixtures of  $H_2$ ,  $CH_4$ ,  $CO$ ,  $CO_2$ ,  $N_2$ ,  $H_2O$ , and  $NH_3$  using a Tesla coil as an energy source. These are carbon yields, which are product yields based on the initial carbon placed in the system. All of the mixtures were sparked for 48 hr. Aside from the likelihood of multiple activations of reactants and products, this rate of energy input is quite high. Thus, a 2 W spark for 48 hr is 173 000 J, or the present atmospheric corona discharge energy ( $12.5 \text{ J cm}^{-2} \text{ yr}^{-2}$ ) available per  $\text{cm}^{-2}$  in 14 000 yr. But the atmosphere above each  $\text{cm}^2$  of the earth's surface contains about 875 l of gas, so it would take  $4 \times 10^6$  years for a given three liter volume (the volume of our reaction vessel) to receive 173 000 J of corona discharge.

A more realistic prebiotic experiment is to remove the products of the activation step so that they are not exposed a second time to the energy source. This is equivalent to transporting the products synthesized in the primitive atmosphere to the ocean, and thereby protecting them from destruction by atmospheric energy sources. Experiments of this type, using lower inputs of energy, give energy yields (moles of product  $\text{J}^{-1}$ ) which can be used to estimate the relative importance of the different energy sources on the primitive earth. This paper will show that energy yields give a considerably different picture than carbon yields when considering various  $CH_4$ ,  $CO$ , and  $CO_2$  atmospheres.

## 2. Experimental

The spark discharge flask previously used to determine carbon yields (Schlesinger and Miller, 1983a, b) was modified by the addition of a thermometer well. The spark was provided by a continuous wave spark generator, Cenco Model 80721. This spark generator was modified for continuous operation by removing part of its Bakelite covering to allow for air circulation and cooling. Several different spark coils were examined with a frequency analyzer which indicated that the differences in power among the different spark coils were due to differences in the magnitude and not the range of frequencies. A spectrum analyzer and broad band oscilloscope showed a peak around 3.5 MHz with overtones detectable to 1000 MHz. The tungsten electrodes were cemented in place with Apiezon Type W sealing compound to minimize the variability of energy input due to differences in the length of the spark gap. The discharge and calibration flasks were insulated with polyurethane. In order to determine the total energy input into a discharge flask, the rise in temperature during the initial stage of a sparking run was compared to that produced by a known amount

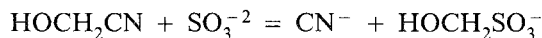
of power from a Hewlett-Packard 25 power supply passing through a Nichrome wire connecting the two electrodes in the calibration flask. The power generated by the spark coils ranged from 2 to 4 W.

Either 25 or 50 ml of water were added to the discharge flask and the air removed via a vacuum manifold system. After allowing sufficient time for the water to degas, the desired gases were introduced into the discharge flask. All reaction mixtures contained 100 torr of  $N_2$  and 100 torr of either  $CH_4$ ,  $CO$ , or  $CO_2$ . The amount of  $H_2$  varied from 0 to 400 torr. All gases were C.P. grade and were used without further purification except for  $CH_4$  and  $CO_2$  which were condensed and distilled.

The discharge flask was insulated after filling and the temperature rise was recorded over a period of 20 min after turning on the spark. At predetermined times, ranging from 1 hr to 11 days, the sparking was stopped and the aqueous phase in the flask stirred for at least two hours to allow equilibration with the gas phase. A small portion of the solution in the flask was then withdrawn with care being taken to prevent air from entering the vessel. The sample was then stored in the refrigerator until analysis. The sparking was continued after the first and succeeding samples were withdrawn without changing the gas phase. Corrections were made for the amounts of HCN and  $H_2CO$  removed with the samples. The rise in temperature and the watts were measured with each restart.

The HCN concentrations in the samples were measured with an Orion cyanide electrode (Model 94-06). Prior to measurement, the pH of the samples were adjusted to 12.7 and dimedone added to complex the formaldehyde (Schlesinger and Miller, 1983b). This technique measures the cyanide present as free HCN and any which is bound in the hydroxynitriles. Only the cyanide occurring as aminonitriles is not measured since the dissociation is slow (Van Trump and Miller, 1981).

The  $H_2CO$  concentrations in the samples were measured with chromotropic acid using the procedure of West and Sen (1956). In order to measure the  $H_2CO$  bound in the glycolonitrile it is necessary to dissociate the glycolonitrile in basic solution, since the nitrile gives a very small color yield with chromotropic acid. At pH 10 and 1M  $SO_3^{2-}$ , the reaction



converts more than 90% of the glycolonitrile to the formaldehyde-sulfite adduct. This adduct decomposes under the acid conditions of the chromotropic acid reaction, giving a full color yield for the formaldehyde. This technique is superior to the method previously used (Schlesinger and Miller, 1983b) of estimating the formaldehyde by the difference in the total HCN and the free HCN.

The major uncertainty in the energy yield determination is the energy of the spark. We estimate the energy yields to be accurate only within a factor of two. There is also an uncertainty of whether different corona discharges give the same energy yields since there is a limited understanding of the nature of the discharges and of the mechanisms of HCN and  $H_2CO$  synthesis.

### 3. Results

The first set of experiments investigated the time course of the production of HCN and  $\text{H}_2\text{CO}$  in three different atmospheres,  $\text{H}_2/\text{CH}_4 = 1$ ,  $\text{H}_2/\text{CO} = 2$ , and  $\text{H}_2/\text{CO}_2 = 3$ . Figure 1 shows the yields of HCN carbon yields vs spark time. Figure 2 shows the  $\text{H}_2\text{CO}$  carbon yields vs spark time.

It is apparent that the relative carbon yields in these three atmospheres shown are dependent on the time taken for comparison, particularly for HCN. The decrease in carbon yields with time, when they might be expected to either increase or level off, could be due to the decomposition of HCN and  $\text{H}_2\text{CO}$  previously synthesized in the spark or by formation of glycine nitrile and other aminonitriles. The aminonitrile concentration was estimated by hydrolyzing the last day's sample and analyzing for amino acids. The measured carbon yields of glycine nitrile (10–20%) suggest that the decline in HCN and  $\text{H}_2\text{CO}$  yields after several days (Figures 1–2) could be accounted for by assuming that they reacted to form glycine nitrile.

In order to avoid the complications caused by long spark times, we estimated the energy yields by extrapolating the yields measured at 1, 3, and 9 hr back to zero time. Figure 3 shows typical extrapolations for three different gas mixtures. The extrapolations with  $\text{CH}_4$  and CO are straight-forward. The  $\text{CO}_2$  mixture shows a substantial increase in yield with time, suggesting that there may be an intermediate between  $\text{CO}_2$  and HCN. Although there may be other possibilities,  $\text{CH}_4$  and CO are reasonable candidates for this intermediate.

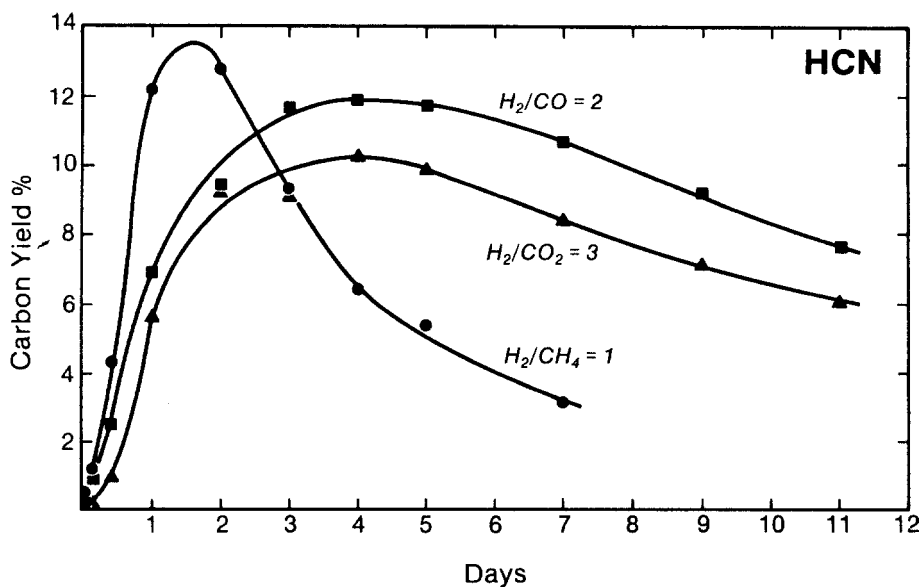


Fig. 1. Time course for the production of HCN for three gas mixtures.

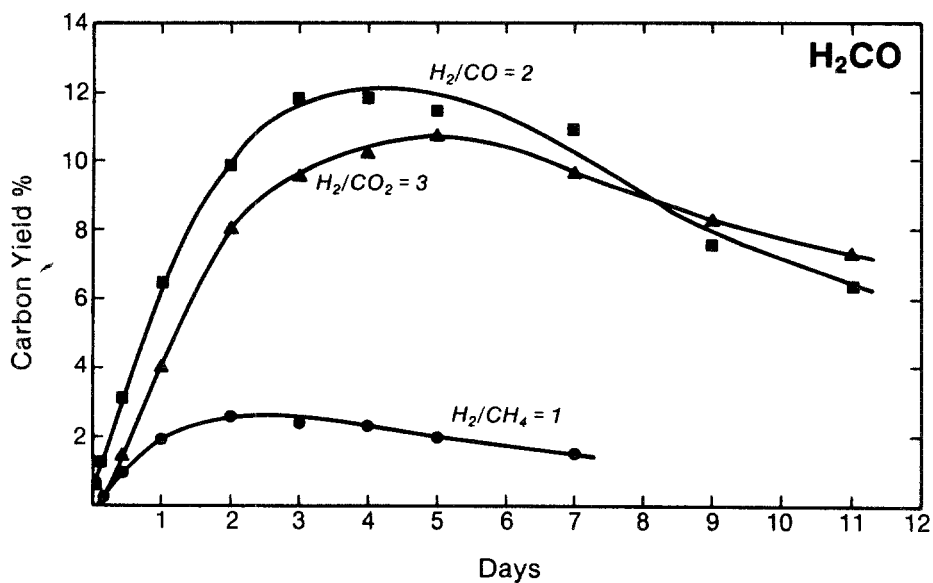


Fig. 2. Time course for the production of H<sub>2</sub>CO for three gas mixtures.

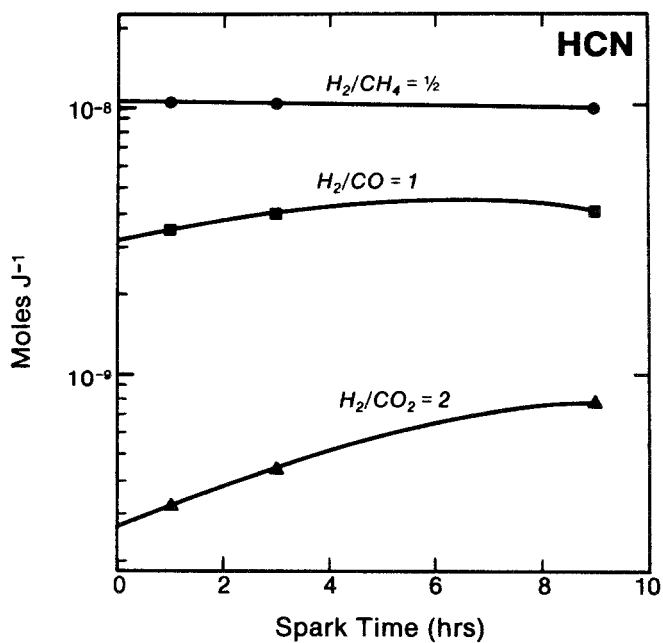


Fig. 3. Extrapolation of energy yields to obtain zero time value.

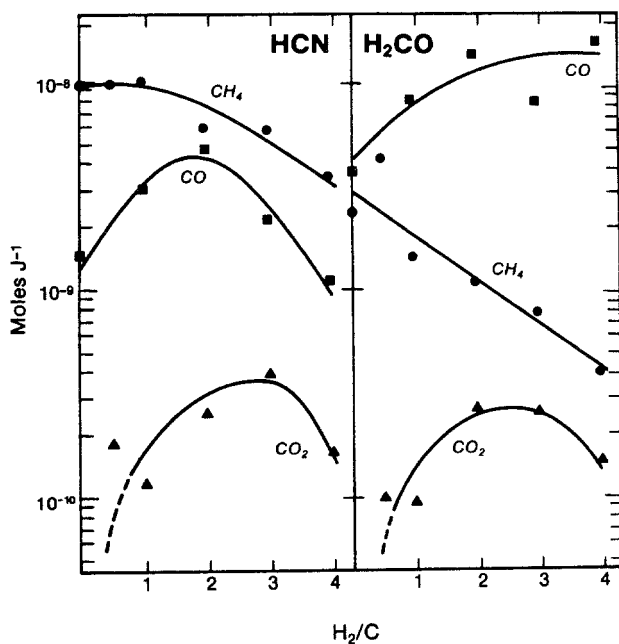


Fig. 4. Zero time energy yields for different  $H_2/C$  ratios.

This study was extended to a range of  $H_2/CH_4$ ,  $H_2/CO$ , and  $H_2/CO_2$  mixtures. Figure 4 shows the energy yields of HCN and  $H_2CO$  for those atmospheres. The energy yields for the production of HCN ranged from 4 to 10 nmoles  $J^{-1}$  in the  $CH_4$  atmospheres, from 1 to 5 nmoles  $J^{-1}$  in the CO atmospheres, and from 0.1 to 0.4 nmoles  $J^{-1}$  in the  $CO_2$  atmospheres. For the production of  $H_2CO$ , the values ranged from 4 to 14 nmoles  $J^{-1}$  in the CO atmospheres, from 0.4 to 4 nmoles  $J^{-1}$  in the  $CH_4$  atmospheres, and from 0.1 to 0.3 nmoles  $J^{-1}$  in the  $CO_2$  atmospheres.

#### 4. Discussion

It is apparent from the results of this study that using carbon yields to compare the relative efficiencies of different atmospheres for the prebiotic production of small molecules can be misleading. The problem is best illustrated in Figure 1, which shows that the carbon yields with different gas mixtures vary widely depending on the sparking time. After sparking for one day, it would appear that the  $CH_4$  atmosphere would be much more efficient than either the CO or  $CO_2$  mixtures. If the samples were taken after seven days of sparking, however, the efficiency of the  $CH_4$  mixture would appear to be much less than the CO and  $CO_2$  mixtures. The previous study of carbon and energy yields (Schlesinger and Miller, 1983 a, b; Miller and Schlesinger, 1984) used a 48 hour sparking period and in those cases the carbon yields

of the  $\text{CH}_4$ ,  $\text{CO}$ , and  $\text{CO}_2$  were about the same except for the fall off at low  $\text{H}_2/\text{CO}$  and  $\text{H}_2/\text{CO}_2$  ratios.

Energy yield data (Figure 4) to suggest quite a different interpretation. While there is an initial increase in the efficiency of  $\text{HCN}$  and  $\text{H}_2\text{CO}$  production with increasing  $\text{H}_2/\text{C}$  in several cases, the general trend is one of decreasing production at high  $\text{H}_2/\text{C}$  ratios. Also, at no  $\text{H}_2/\text{C}$  ratio do the yields generated from the  $\text{CO}_2$  atmospheres reach the yields produced by the  $\text{CH}_4$  and  $\text{CO}$  atmospheres. It is of interest to note that  $\text{CH}_4$  is more efficient than  $\text{CO}$  in  $\text{HCN}$  production while the reverse is true for the synthesis of  $\text{H}_2\text{CO}$ .

The principle variable examined in these experiments was the  $\text{H}_2/\text{C}$  ratio. Other variables such as temperature, pressure and the mole fractions of the gases were not examined and might affect the energy yields, with the mole fractions probably being the most important.

### 5. Comparisons with Previous Discharge Experiments

There are only a few previous reports of  $\text{HCN}$  and  $\text{H}_2\text{CO}$  syntheses in which energy yields can be estimated. Experiments using a silent electric discharge and a flow system gave  $\text{HCN}$  carbon yields from  $\text{CH}_4 + \text{N}_2$  as high as 36% and estimated energy yields as high as 27 nmoles  $\text{J}^{-1}$  (Toupance *et al.*, 1975). The corresponding carbon and energy yields from  $\text{CH}_4 + \text{NH}_3$  were 30% and 27 nmoles  $\text{J}^{-1}$ . Similar yields (26 nmoles  $\text{J}^{-1}$ ) were obtained using a radio frequency-induced plasma (Capezzuto *et al.*, 1973). These are in apparent agreement with our yields of about 10 nmoles  $\text{J}^{-1}$ .

Briner and co-workers conducted an extensive investigation of  $\text{HCN}$  synthesis using  $\text{CH}_4 + \text{NH}_3$ ,  $\text{CH}_4 + \text{N}_2$  and  $\text{CO} + \text{N}_2 + \text{H}_2$  mixtures (Briner and Baerfuss, 1919; Briner *et al.*, 1938; Briner and Hoefler, 1940). Most of their yields are in the range of 4.7 to 96 nmoles  $\text{J}^{-1}$ , although a few high frequency experiments gave yields as high as 382 nmoles  $\text{J}^{-1}$ . Briner's experiments were done to optimize yields for industrial synthesis, so it would be surprising if such high yields were possible under geological conditions.

Thornton and Sergio (1967) used a high frequency discharge on mixtures of  $\text{CH}_4$  and  $\text{H}_2\text{O}$ . The yield of  $\text{H}_2\text{CO}$  was about 13 nmoles  $\text{J}^{-1}$  when the product was protected by absorption in liquid water after synthesis. The yield was about 1/3 of this without absorption. Koenig and Weinig (1927) used a flow discharge on mixtures of  $\text{CO}$  and  $\text{H}_2$  and obtained a yield of 18 nmoles  $\text{J}^{-1}$ . Mourey *et al.*, (1981) and Boscard and Toupance (1981) used a spark discharge on a  $\text{CH}_4$  and water mixture and obtained a yield of only 0.29 nmoles  $\text{J}^{-1}$ . This yield was increased to 3 nmoles  $\text{J}^{-1}$  when liquid water was present to absorb the  $\text{H}_2\text{CO}$  (F. Raulin, personal communication; Mourey, 1982).

### 6. A Balance Sheet for $\text{HCN}$ Synthesis on the Primitive Earth

A balance sheet for the production of small molecules on the primitive Earth can be

prepared by combining the energy yields from different sources with the energy available from those sources. The generally accepted values for energy available from lightning and corona discharge are  $4.2$  and  $12.6 \text{ J cm}^{-2} \text{ yr}^{-1}$ , respectively (Miller *et al.*, 1976).

There are few data available for HCN production by lightning. A calculation by Chameides and Walker (1981) gives energy yields for the production of HCN and NO from lightning bolts for various mixtures of  $\text{N}_2$ ,  $\text{CH}_4$ , CO,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$ . The calculations were based on the effects of the post-flash shock wave, which raises the region near the lightning bolt to a high temperature, followed by cooling and quenching of the high temperature equilibrium mixture of products at the freeze-out temperature (2000 to 2500 K for HCN). Their calculations show that the yield of HCN depends mainly on the O/C ratio in the presence of excess  $\text{N}_2$ , where O is the total oxygen ( $\text{CO} + 2\text{CO}_2 + \text{H}_2\text{O}$ , etc.) and C is the total carbon ( $\text{CH}_4 + \text{CO} + \text{CO}_2$ ). The calculated yields do not depend strongly on the H/C ratio. The yields of HCN in  $\text{CH}_4$  atmospheres are about  $530 \text{ nmoles J}^{-1}$ . In CO atmospheres the yield of HCN falls off to about  $0.153 \text{ nmoles J}^{-1}$ , and in  $\text{CO}_2$  atmospheres the yield is calculated to be only about  $0.00042 \text{ nmoles J}^{-1}$ .

The spark discharge energy yields fall off much less in the sequence  $\text{CH}_4$ , CO and  $\text{CO}_2$  as shown in Figure 4. These experimental results are not in contradiction to the lightning calculations since sparks and other electrical discharges are different in character from lightning bolts and their associated shock waves. These differences include production of HCN in electric discharges at O/C ratios where little HCN production is calculated in lightning bolts, synthesis of substantial amounts of  $\text{NH}_3$ , and a major role for  $\text{H}_2$  in the HCN yields in electric discharges. In addition, formaldehyde would not be synthesized at all in the high temperature region of a lightning bolt. The role of shock waves is apparently minimal in the spark, the effective temperature of the spark being much lower than lightning, and ion-molecule and radical reactions appear to play a more important role in the products produced by the spark than in the frozen high temperature equilibrium of lightning. It is possible that additional products with lower freeze-out temperatures can be made in lightning bolts by reactions not considered by Chameides and Walker.

A preliminary measurement of the HCN energy yield from artificial lightning was obtained at Ames Research Center in collaboration with C. McKay and T. Scattergood. In a  $\text{CH}_4$  atmosphere, we measured an HCN energy yield of  $31 \text{ nmoles J}^{-1}$ . This is an order of magnitude lower than the calculated yield. The energy yields in four CO atmospheres ranged from about  $0.002$  to  $0.05 \text{ nmoles J}^{-1}$  and the yields in four  $\text{CO}_2$  atmospheres ranged from about  $0.003$  to  $0.006 \text{ nmoles J}^{-1}$ . The yields with CO and  $\text{CO}_2$  are quite uncertain because the HCN measurements were near the limit of sensitivity of the cyanide electrode.

There has also been some work done using energy generated by expanding gases in shock wave tubes. Rao *et al.* (1967) investigated HCN synthesis from various hydrocarbons and  $\text{N}_2$  in high temperature shock experiments. HCN carbon yields were about 15% for temperatures greater than 3000 K. The energy yields from these



experiments [calculated by Bar-Nun and Shaviv (1975)] were 332 nmoles  $J^{-1}$ .

A photochemical source of HCN has been proposed by Zahnle (1986). Nitrogen atoms are produced by the Lyman continuum (796 to 912 Å) and diffuse lower into the atmosphere to react with  $CH_2$  and  $CH_3$ , producing HCN. The yields of HCN range between a maximum of 520 nmoles  $cm^{-2} yr^{-1}$  when the production of N atoms is limiting and 5 to 50 nmoles  $cm^{-2} yr^{-1}$  at lower  $CH_4$  fluxes.

Inspection of the estimates discussed in this section, as well as the results of our experiments, shows that the HCN production rates from the various sources are comparable within an order of magnitude. This suggests that errors in any particular estimate will not affect the value chosen for model calculations.

### 7. A Balance Sheet for $H_2CO$ Synthesis on the Primitive Earth

The balance sheet for the production of formaldehyde is limited to that which may be produced from either spark discharge or UV light. No  $H_2CO$  is generated in lightning bolts either in calculations (Chameides and Walker, 1981) or in our limited measurements of the samples generated from artificial lightning.

The data of Ferris and Chen (1975) can be used to estimate energy yields for the production of  $H_2CO$  from the action of UV light on a  $CH_4$  atmosphere of about 3 nmoles  $J^{-1}$ . Experimental values for CO atmospheres range from about 4 nmoles  $J^{-1}$  (Bar-Nun and Hartman, 1978) to 13 nmoles/J (Bar-Nun and Chang, 1983).

The production rate of  $H_2CO$  in a model  $CO_2$  atmosphere has been calculated by Pinto *et al.* (1980). The rain out rate is about 15 nmoles  $cm^{-2} yr^{-1}$ . The assumed atmosphere is relatively reducing since  $H_2/CO_2 = 3$ . Another calculation by Kasting *et al.* (1984) gives 1.6 to 45 nmoles  $cm^{-2} yr^{-1}$ . An important part of these calculations is the rain out rate of the  $H_2CO$ , since  $H_2CO$  absorbs U.V. at 3200 Å. It is not clear whether this factor has been adequately treated. As in the case with HCN, the  $H_2CO$  production rates from the various sources, including the results of our experiments, are generally comparable.

### 8. The Concentration of HCN in the Primitive Ocean

These production rates of HCN allow a calculation of the steady state concentration in the primitive ocean. We assume that all the HCN produced in the atmosphere enters the ocean and remains there and that the only pathway for the loss of HCN is hydrolysis to formamide and then to formic acid. At steady state, the production rate ( $S_{HCN}$  in moles  $cm^{-2} yr^{-1}$ ) equals the rate of hydrolysis

$$S_{HCN} = \frac{d(HCN)}{dt} V_0,$$

where (HCN) is the molar concentration, and  $V_0$  is the volume of the ocean in liters  $cm^{-2}$ , now 300  $l cm^{-2}$ . Writing the hydrolysis rate of HCN as a pseudo first-order reaction

$$-\frac{d(\text{HCN})}{dt} = k_1 (\Sigma \text{HCN}),$$

where  $k_1$  is the pseudo first-order rate constant in  $\text{yr}^{-1}$  and depends on temperature and pH, and  $\Sigma \text{HCN} = \text{HCN} + \text{CN}^-$ .

The hydrolysis of HCN is both acid and base catalyzed. The acid catalyzed reaction has been investigated mostly in 2 to 10 M HCl and  $\text{H}_2\text{SO}_4$  (Krieble and Noll, 1939; Rabinovitch and Winkler, 1942) and at 0.1 to 1M  $\text{HNO}_3$  (Miller, unpublished). The rate is

$$-\frac{d(\text{HCN})}{dt} = k_2^{\text{H}^+} (\text{H}^+) (\text{HCN}) \quad (1)$$

with an approximate value of  $k_2^{\text{H}^+}$  given by

$$\log k_2^{\text{H}^+} (\text{yr}^{-1}) = 12.76 - 4720/T.$$

The rate of the base catalyzed hydrolysis is

$$\begin{aligned} -\frac{d(\text{HCN})}{dt} &= k_2^{\text{OH}^-} (\text{OH}^-) (\text{HCN}) \\ &= \frac{k_2^{\text{OH}^-} K_w (\Sigma \text{HCN})}{(\text{H}^+) + K_{\text{HCN}}}, \end{aligned} \quad (2)$$

where  $k_2^{\text{OH}^-}$  is the second order rate constant of  $\text{OH}^-$  hydrolysis,

$$K_{\text{HCN}} = (\text{H}^+)(\text{CN}^-)/(\text{HCN}), \quad K_w = (\text{H}^+) (\text{OH}^-).$$

We use  $\text{p}K_w$  from Robinson and Stokes (1959) and  $\text{p}K_{\text{HCN}}$  from Schlesinger and Miller (1973).

$$\text{p}K_w = -6.0846 + 4471.33/T + 0.017053T,$$

$$\text{p}K_{\text{HCN}} = -8.85 + 3802/T + 0.01786T.$$

The value of  $k_2^{\text{OH}^-}$  can be obtained from the data reported by Sanchez *et al.* (1967) and Miller (unpublished)

$$\log k_2^{\text{OH}^-} (\text{day}^{-1}) = 16.62 - 4440/T.$$

In the pH region 6–9, Equation (2) is applicable with the acid catalyzed pathway making a negligible contribution. Equating the production rate and hydrolysis of HCN gives

$$\Sigma \text{HCN} = \frac{S}{V_0} \frac{[(\text{H}^+) + K_{\text{HCN}}]}{k_2^{\text{OH}^-} K_w} = \frac{S}{V_0 k_1}. \quad (3)$$

Taking  $S = 100 \text{ nmoles cm}^{-2} \text{ yr}^{-1}$  and  $V_0 = 300 \text{ l cm}^{-2}$  we get the half lives and concentrations in Table I.

TABLE I

Half-lives and concentrations of HCN in the primitive ocean based on a HCN production rate of  $100 \text{ nmoles cm}^{-2} \text{ yr}^{-1}$  and an ocean volume of  $300 \text{ cm}^{-2}$

		0 °C	25 °C	50 °C
$t_{1/2}$ (yr)	pH8	7000	40	0.5
$t_{1/2}$ (yr)	pH7	70000	400	5
$M_{\text{HCN}}$	pH8	$4 \times 10^{-6}$	$2 \times 10^{-8}$	$3 \times 10^{-10}$
$M_{\text{HCN}}$	pH7	$4 \times 10^{-5}$	$2 \times 10^{-7}$	$3 \times 10^{-9}$

Equation (3) shows that the concentration of HCN will be increased proportionally to the production rate and to the  $(\text{H}^+)$ , an inversely to the volume of the ocean. The results of Table I make it clear that low temperatures and pH favor higher concentrations of HCN, but even at pH7 and  $0^\circ$  a concentration of  $3.5 \times 10^{-5} \text{ M}$  is much lower than the usual prebiotic experiment. Concentrations of HCN of  $10^{-6} \text{ M}$  are sufficient to make amino acids by the Strecker synthesis (Miller and Van Trump, 1981) but adenine synthesis would require a concentration mechanism, with freezing being the most likely (Sanchez *et al.*, 1967).

The spark discharge synthesis of HCN would have been only  $1 \text{ nmole cm}^{-2} \text{ yr}^{-1}$  for  $\text{H}_2/\text{CO}_2 = 1$  and  $4 \text{ nmoles cm}^{-2} \text{ yr}^{-1}$  for  $\text{H}_2/\text{CO}_2 = 4$ , which is considerably lower than the  $100 \text{ nmoles cm}^{-2} \text{ yr}^{-1}$  assumed in this calculation. This would lead to HCN concentrations 25 to 100 times lower than given in Table I, which might raise problems for amino acid and purine synthesis. If the Zahnle N atom synthesis were as efficient on the primitive earth as calculated, then this problem would not arise.

### 9. The Concentration of Amino Acids in the Primitive Ocean

The production rates of HCN and  $\text{H}_2\text{CO}$  estimated above permit us to calculate the rate of build up of amino acids in the primitive ocean and their steady state concentration. Provided the concentrations of HCN and aldehydes do not drop too low, the Strecker synthesis will be effective in the primitive ocean (Miller and Van Trump, 1981). We will assume an amino acid yield of 10% based on the HCN production. This is the approximate yield reported with  $\text{CH}_4$ , CO and  $\text{CO}_2$  atmospheres (Schlesinger and Miller, 1983 a, b). The yield is much higher ( $\sim 90\%$ ) with the Strecker synthesis, while the cyanide polymerization gives only about 1% (Lowe *et al.*, 1963; Ferris *et al.*, 1978).

Taking a combined HCN production rate of  $100 \text{ nmoles cm}^{-2} \text{ yr}^{-1}$ , the steady state amino acid production rate would then have been  $10 \text{ nmoles cm}^{-2} \text{ yr}^{-1}$ . Taking the volume of the ocean as  $300 \text{ cm}^{-2}$ , the increase in amino acid concentration

would have been  $3.3 \times 10^{-11}$  moles  $\text{yr}^{-1}$ . Assuming no losses, this gives  $3.3 \times 10^{-4}$  M in 10 million years. In a low temperature ocean the losses from thermal decomposition should be low for amino acids such as glycine and alanine but considerably greater for less stable amino acids such as serine. The losses from adsorption on clays, ionizing radiation and ultraviolet light are much more difficult to estimate. The most important loss mechanism was probably the submarine vents, in which the sea water is heated to at least  $350^\circ$  thereby decomposing all the amino acids. Since the entire ocean on the average passes through the vents in 10 million years (Edmond *et al.*, 1982), the amino acid concentration could not have risen higher than  $3 \times 10^{-4}$  M with the above assumptions. Increasing the production rate of HCN or decreasing the size of the ocean would increase proportionally the steady state concentration of amino acids.

As discussed for the HCN production,  $\text{CO}_2$  atmospheres give considerably lower HCN yields from spark discharges. Without the HCN production from the Zahnle N atom mechanism, the amino acid concentrations would be 25 to 100 times lower than the  $3 \times 10^{-4}$  M. There is no way at the present time to estimate the amino acid concentration needed for life to arise. A molarity of  $3 \times 10^{-4}$  seems substantial and a factor of 100 or 1000 lower seems almost too small. A detailed mechanism of the process leading to the origin of life is needed to place constraints on the amino acid concentration as well as the atmosphere conditions and composition required for the synthesis of necessary amino acids.

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