CARBON AND ENERGY YIELDS IN PREBIOTIC SYNTHESES USING ATMOSPHERES CONTAINING CH_4, CO AND CO_2

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ABSTRACT

Yields based on carbon are usually reported in prebiotic experiments, while energy yields (moles cal^{-1}) are more useful in estimating the yields of products that would have been obtained from the primitive atmosphere of the earth. Energy yields for the synthesis of HCN and H_2CO from a spark discharge were determined for various mixtures of CH_4, CO, CO_2, H_2, H_2O, N_2 and NH_3. The maximum yields of HCN and H_2CO from CH_4, CO, and CO_2 as carbon sources are about 4×10^{-8} moles cal^{-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 were 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 organization of these polymers.

Types of organic compounds in the primitive oceans will be determined by such factors as the composition of the atmosphere, the sources of energy to activate the atmospheric constituents, the further reactions which occur in the oceans, and the rate of decomposition of the 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 was only a single kind of energy and the synthesis of organic

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compounds was not limited by the available energy. However, there were a number of sources of energy on the primitive earth, as has been extensively discussed (1) and prebiotic synthesis was probably limited by the total quantity of carbon available in the atmosphere rather than by the energy available from the various sources.

With multiple sources of energy, the yields of a particular compound are the product of the efficiency of the energy source (in moles synthesized cal^{-1}) and the energy available in the source (in cal cm^{-2} yr^{-1} of the earth's surface). This applies whether the prebiotic synthesis is energy limited or carbon limited. In case of high partial pressures of CH_4, CO or CO_2 where the system is energy limited, the product of the efficiency and the quantity of the energy source clearly gives the yields. When the partial pressure of the carbon source is very low, the same equation applies. However, the efficiency of the energy source may fall off considerably since the energy may be expanded in excitation of nitrogen or other "inert" atmospheric constituents rather than in activating the carbon. Thus the energy yield of HCN (per cal) from a lightning bolt will be less when pCH_4 is 10^{-6} atm than when it is 0.1 atm. The percent yield of HCN based on the carbon might be nearly constant since the HCN yield would depend on C/N/O ratios of the atmosphere near the lightning bolt and not on the partial pressures of the gases.

CARBON YIELDS IN ATMOSPHERES CONTAINING CH_4, CO AND CO_2

Before discussing energy yields, we will first review our recent results using a spark discharge on various mixtures of H_2, CH_4, CO, CO_2, N_2 and NH_3.

In these experiments the yields of amino acids were determined (2) as well as the yields of hydrogen cyanide, formaldehyde, ammonia, and urea (3). We will discuss here only the HCN and H_2CO yields since these are the precursors to the purines, some amino acids and the sugars. Comparing amino acid yields does not give an accurate indication of the efficiency of an energy source, since the amino acids require the synthesis of both the aldehyde and HCN as well as the reaction conditions for an efficient Strecker synthesis.

Figure 1 gives the HCN yields from various mixtures of CH_4, CO and CO_2. The conditions are given in the legend. The HCN yields refer to the sum of free HCN, HCN contained in glycolonitrile and other hydroxynitriles, and the HCN contained in glycine nitrile and other amino nitriles. The figure shows that HCN yields are about the same for the CH_4 experiments as for experiments with $H_2/CO > 1.0$ and $H_2/CO_2 > 2.0$. The yields are greater in the absence of added NH_3 (added as 0.05 M NH_4Cl) than

in its presence. At low H_2/CO ratios the yield of HCN drops off somewhat, but at low H_2/CO_2 ratios the yield drops off so much that useful quantities of HCN would not be available on the primitive earth under these conditions.

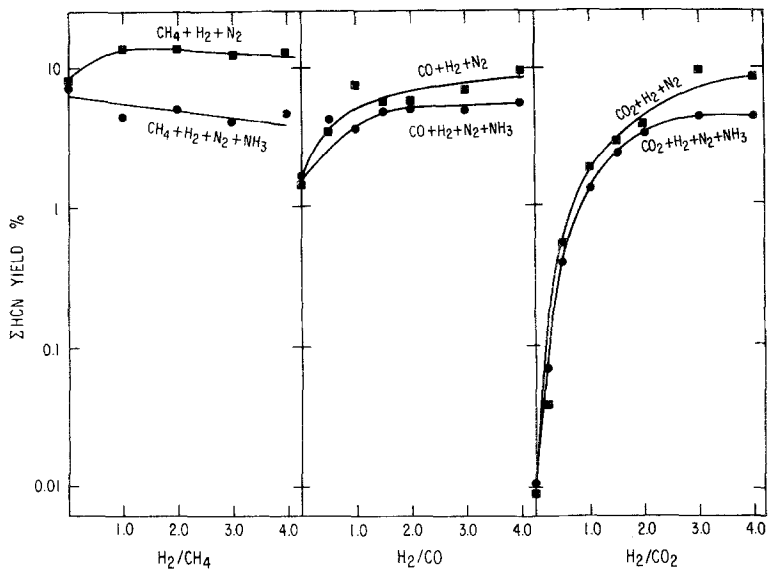

Figure 1. Total HCN yields based on carbon. $\Sigma HCN = (HCN)_{free}$ + glycolonitrile + other hydroxy nitriles + glycine nitrile + other amino nitriles. The spark discharge apparatus consists of a modified 3-liter flask with two removable tungsten electrodes and a stopcock. The spark generator is a Tesla coil in contact with one of the tungsten electrodes. In all experiments pN_2 = 100 torr, and pCH_4 or pCO, or pCO_2 = 100 torr. For experiments containing NH_3, the spark discharge flask contained 100 ml 0.05 M NH_4Cl brought to pH 8.7 so that pNH_3 was 0.1 torr. For experiments not containing NH_3, the flask had 100 ml of H_2O. The flask was kept at room temperature, and the spark generator was operated continuously for 48 hrs.

Figure 2 shows the formaldehyde yields in the same set of experiments. The H_2CO yields refer to the sum of free H_2CO, plus the H_2CO contained in glycolonitrile and glycine nitrile. The H_2CO yields show the same pattern as the HCN yields, but the CH_4 experiments produced an excess of HCN, and the CO and CO_2 experiments all produced an excess of H_2CO.

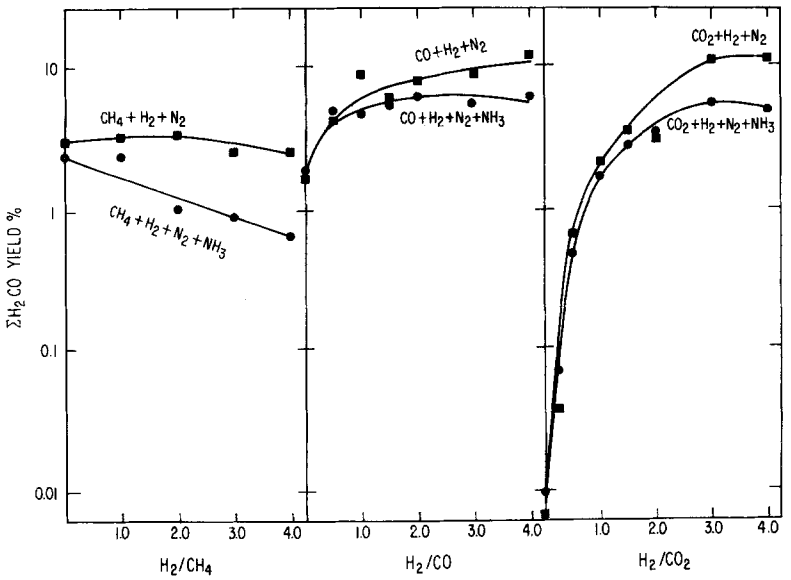

Figure 2. Total formaldehyde yields based on carbon. H_2CO = $(H_2CO)_{free}$ + glycolonitrile + glycine nitrile. The conditions are the same as in Fig. 1.

It is to be noted from the sum of the HCN and H_2CO yields that conversion of between 10 and 20% of the carbon occurred for the CH_4, $H_2/CO > 1$ and $H_2/CO_2 > 2$ experiments. These are among the highest carbon yields in the prebiotic experiments and demonstrate the efficient synthesis by electric discharges.

ENERGY YIELDS

There are insufficient data available to make a comprehensive discussion of energy yields, but some of the available data will be examined here. The carbon yield results reported in the above exeriments can be converted to energy yields by measuring the energy of the spark. This was determined calorimetrically by insulating the flask and measuring the temperature rise produced within by passage of the spark for a period of several hours. The heat capacity of the apparatus was calibrated with the measured temperature rise produced by a Nichrome wire connected to the two tungsten electrodes, which were connected to a constant voltage source. The current was measured with an ammeter. The spark generator delivers 1.0 ± 0.2 watts of power to the flask. The primary power input to the spark generator is about 50 watts, so the spark source is about 2% efficient.

An input power of 1 watt in the spark corresponds to 41,300 cal in 48 hrs. About 1.6×10^{-3} moles (i.e. a 10% yield of the 16 mmoles of CH_4 in the flask) of HCN were synthesized in this 48 hrs in the most efficient of the CH_4, CO and CO_2 experiments. Thus the energy yield is 3.9×10^{-8} moles cal^{-1}. If we use a figure of 3 cal cm^{-2} yr^{-1} for corona discharge on the earth (1), then the best syntheses with CH_4, CO and CO_2 give 11.6×10^{-8} moles cm^{-2} yr^{-1} for HCN and for H_2CO. The energy yield is probably higher than this because HCN synthesis was nearly complete after 48 hrs. A better energy yield would probably be obtained using shorter sparking periods.

Experiments using a silent electric discharge and a flow system (4) gave HCN carbon yields from $CH_4 + NH_3$ as high as 30%. We calculate their energy yields to be as high as 13.4×10^{-8} moles cal^{-1}. Similar yields (11×10^{-8} moles cal^{-1}) were obtained by Capezzuto et al. (5) using a radiofrequency-induced plasma. These are in apparent agreement with our yields of 4×10^{-8} moles cal^{-1} when the higher yields expected from a flow system are taken into account.

Briner and co-workers (6-8) conducted an extensive investigation of HCN synthesis using $CH_4 + NH_3$, $CH_4 + N_2$ and $CO + N_2 + H_2$ mixtures. Most of their yields are in the range of 2×10^{-8} to 40×10^{-8} moles cal^{-1}, although a few high frequency experiments gave yields as high as 160×10^{-8} moles cal^{-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.

There are no experimental data available for the efficiency of a lightning bolt for HCN synthesis. A calculation by Chameides and Walker (9) gives HCN and NO yields from various mixtures of N_2, CH_4, CO, CO_2 and H_2O. The calculation is 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 (2,000 to 2,500°K for HCN). Their calculation shows that the yield of HCN depends mainly on the O/C ratio in the presence of excess N_2, where O is the total oxygen ($CO + 2CO_2 + H_2O$ etc.) and C is the total carbon ($CH_4 + CO + CO_2$). The yield is not sensitive to the H/C ratio. This result can be understood in terms of a series of reactions that go essentially to completion. The first reaction is

$$C + O \longrightarrow CO \ .$$

Any O in excess of the C forms NO

$$N + O \longrightarrow NO \quad ,$$

and any C in excess of the O forms HCN

$$C + N + H \longrightarrow HCN \quad .$$

The calculated yields of HCN for $O/C < 0.67$ are about 10^{-17} molecules/Joule or 4×10^{-8} moles cal^{-1} which is the same as our experimental energy yield with the spark. The yield falls off drastically at higher O/C ratios, being 0.004×10^{-8} moles cal^{-1} for $O/C = 1$ corresponding to CO, and 4×10^{-14} mole cal^{-1} for $O/C = 2$ corresponding to CO_2. The present atmosphere has a corona discharge/lightning ratio of 3, and if this was the ratio on the primitive earth, then the spark discharge synthesis would have been slightly more important than lightning.

Although there have been no experiments with artifical lightning bolts in reduced atmospheres, there has been some work using shock waves generated by expanding gases in shock wave tubes. Rao et al. (10) investigated HCN synthesis from various hydrocarbons and N_2 in high temperature shock experiments. HCN carbon yields were about 15% for shock temperatures greater than 3,000°K. The energy yields from these experiments (calculated by Bar-Nun and Shaviv (11)) were 2×10^{10} molecules erg^{-1} or 8×10^{-8} moles cal^{-1}. This is a factor of two higher than Chameides and Walker's calculation (9), but the two can be considered essentially in agreement. The shock wave tube experiments of Bar-Nun et al. (12) and Barak and Bar-Nun (13) measured amino acid production but not the yields of HCN.

It is to be noted that spark and other electrical discharges are different in character and effect from lightning bolts and their associated shock waves. These differences include production of HCN in electric discharges at C/O ratios where little HCN production is calculated in lightning bolts, and synthesis of substantial amounts of NH_3, and a major role for H_2 in the HCN yield 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 wave heating is minimal in the spark, the effective temperature of the spark is much lower than the lightning bolt, 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 the lightning bolt. 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 (9).

The yield of formaldehyde in our electric discharge experiments was about the same as the HCN, i.e. 10% based on the carbon. The energy yield, therefore, is also 3.9×10^{-8} moles cal^{-1}. Thornton and Sergio (14) used a high frequency discharge on mixtures of CH_4 and water. The yield of H_2CO was 1.4 gm/kw-hr or 5.4×10^{-8} moles cal^{-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 (15) used a flow discharge on mixtures of CO and H_2 and obtained a yield of H_2CO of 2 gm/kw-hr or 7.7×10^{-8} moles cal^{-1}. Toupance and co-workers (16,17) used a spark discharge on a $CH_4 + H_2O$ mixture and obtained a H_2CO yield of only 0.12×10^{-8} moles cal^{-1}. The reason for the low yield is probably their use of a static system where the discharge decomposed some of the H_2CO after synthesis, as well as their system being carbon rather than energy limited.

This review of HCN and H_2CO energy yields from several types of electric discharges shows that they are mostly in the range of 4×10^{-8} to 20×10^{-8} moles cal^{-1}, although a few of the industrial type synthesis are higher. The reported yields of H_2CO range from 4×10^{-8} to 8×10^{-8} moles cal^{-1}. Of course, lower yields are possible with a poor gas mixture (e.g. $H_2/CO_2 = 0$) or from the product being destroyed by the spark after synthesis.

Further work on energy yields from the spark discharge will be taken up in a later paper as well as a discussion of yields from various photochemical processes.

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