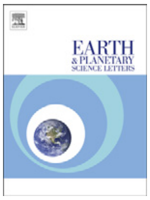
Earth and Planetary Science Letters 308 (2011) 417–423

Contents lists available at ScienceDirect

Earth and Planetary Science Letters

journal homepage: www.elsevier.com/locate/epsl



Revisiting HCN formation in Earth's early atmosphere

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ARTICLE INFO

Article history:
Received 31 January 2011
Received in revised form 12 June 2011
Accepted 14 June 2011
Available online 6 July 2011

Editor: T. Spohn

Keywords:
early earth
HCN
photochemistry
ammonia

ABSTRACT

Using a new photochemical model, the HCN chemistry in Earth's early atmosphere is revisited. We find that HCN production in a CH_4-rich early atmosphere could have been efficient, similar to the results of a previous study (Zahnle, 1986). For an assumed CH_4 mixing ratio of 1000 ppmv, HCN surface deposition increases from $2\times10^9\ cm^{-2}\ s^{-1}$ at $fCO_2=3\%$ to more than $1\times10^{10}\ cm^{-2}\ s^{-1}$ (30 Tg/yr) at $fCO_2=0.3\%$ and 1%. These conditions may well have applied throughout much of the Archean eon, 3.8–2.5 Ga. Prior to the origin of life and the advent of methanogens, HCN production rates would likely have been at $1\times10^7\ cm^{-2}\ s^{-1}$ or lower, thereby providing a modest source of HCN for prebiotic synthesis.

1. Introduction

Zahnle (1986) proposed that atmosphere chemistry between methane photolysis products (CH_3 and $^3CH_2$) and atomic nitrogen can produce hydrogen cyanide, HCN, which is an important molecule in prebiotic chemistry and a potentially important source of fixed nitrogen to the early biosphere. This mechanism depends on the availability of methane in Earth's early atmosphere, which could have been scarce prior to the origin of life (Kasting, 1993). The methane source on prebiotic Earth is discussed in the following section. Once formed, HCN could have been transported to the surface where its hydrolysis product, ammonium ion, may have become a source of ammonia (a strong greenhouse gas) to the atmosphere (Bada and Miller, 1968). Recently, Wolf and Toon (2010) proposed that ammonia in Earth's early atmosphere could have been shielded from photolysis by fractal organic haze particles, with optical properties similar to those discovered in Titan's atmosphere (Wolf and Toon, 2010). This reopens the possibility that ammonia could have helped warm up early Earth. However, the source of ammonia was not specified in their paper. HCN chemistry in Earth's early atmosphere could conceivably have provided this missing ammonia source, helping to solve the faint young Sun problem (Sagan and Mullen, 1972). Our understanding of photochemistry has improved over the past 25 yr, and thus it is necessary to check the validity of the Zahnle, 1986 results.

Early Earth was exposed to an intense solar EUV photon flux (Ribas et al., 2005) which would have produced atomic nitrogen through chemistry in the thermosphere and ionosphere. These N atoms would have flowed down into the lower atmosphere where they would have reacted with the byproducts of methane photochemistry (Zahnle, 1986). Kharecha et al. (2005) showed that methane concentration in early Earth atmosphere could have accumulated to ~1000 ppmv level after methanogens emerged, so methane photochemistry would have been vigorous. In such an environment HCN could then have been formed through the following two reactions:

$$CH_3+N\rightarrow HCN+H_2$$

$$^3CH_2+N\rightarrow HCN+H$$

and the HCN production rate could have reached $10^{10}\ cm^{-2}\ s^{-1}$ (Zahnle, 1986), equivalent to more than 30 Tg/yr. This is comparable to or greater than the NO flux produced in volcanic lightning (Navarro-Gonzalez et al., 1998) impact plumes (Kasting, 1990), thunderstorm lightning (Navarro-Gangzalez et al., 2001), coronal discharge (Nna-Mvondo, 2005), or to reduced nitrogen produced in hydrothermal system (Brandes et al., 1998) or delivered by comets (Chyba and Sagan, 1992). Factors restricting efficient HCN formation are that: 1) the second reaction, which was predicted to be more important than the first reaction (Zahnle, 1986 could be slow

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doi:10.1016/j.epsl.2011.06.011

(Navarro-Gangzalez et al., 2001); and 2) the stratosphere and mesosphere of early Earth would have to have undergone much more efficient vertical mixing than does Earth's present atmosphere in order for significant amounts of HCN to reach the surface (Zahnle, 1986). Thus, both the HCN formation rate and its surface deposition flux on early Earth have been considered as highly uncertain (Navarro-Gangzalez et al., 2001).

Formation of HCN from CH_3 was considered to be slow in Zahnle (1986) because CH_3 production from CH_4 photolysis was not included in that model. More recent experiments (Wang et al., 2000) show that 29% of methane photolysis at Lyman-α leads to methyl radicals (CH_3), and 58% leads to singlet methylene ($^1CH_2$), which can be collisionally de-excited to triplet methylene ($^3CH_2$). Thus, we expect that the formation of HCN from CH_3 and $^3CH_2$ will change from that in the Zahnle model. More importantly, it is known now that the reaction between CH_3 and atomic nitrogen produces H_2CN much more efficiently than HCN and that H_2CN can form HCN through multiple channels (Yung and DeMore, 1999). Recent observations and modeling of nitrogen-containing molecules in Titan's atmosphere (Krasnopolsky, 2009, Yelle et al., 2010 and references therein) provide the opportunity to check these reaction rates and reaction pathways. Here, we apply new knowledge to reinvestigate the HCN chemistry in Earth's early atmosphere. The key questions we ask are 1) could HCN be formed efficiently in early Earth's atmosphere? and 2) what is the relationship between HCN surface deposition flux and the CO_2 and methane mixing ratios in early Earth's atmosphere?

2. Constraints on archean atmosphere composition

Estimating the source of HCN on the early Earth requires that one make assumptions about early atmospheric composition. The three gasses that would have had the most effect on HCN are CO_2, CH_4, and H_2. Oxidized gasses such as O_2 would also have been important, but the concentrations of these gasses can be predicted by our photochemical model.

Consider CO_2 first. The pre-industrial atmospheric CO_2 level (not including anthropogenic enhancement) was ~278 ppmv, or 2.78×10^{-4} bar, which we define as 1 PAL (times the Present Atmospheric Level). At 2.8 Ga, ~100 PAL of CO_2 would have been needed to reach the global mean surface temperature of present-day Earth (288 K), if CO_2 and H_2O were the sole greenhouse gasses (Haqq-Misra et al., 2008; Kasting, 1987; von Paris et al., 2008). On the other hand, published analyses of geochemical data suggest CO_2 concentrations during the Archean in the range from ~3 PAL (Rosing et al., 2010) to <100 PAL (Rye et al., 1995). The rather strict upper limit of 3 PAL atmospheric CO_2 from Rosing et al. is based on the coexistence of magnetite and siderite in banded iron-formations (BIFs). Whether or not this analysis is valid depends on whether sufficient organic matter was available to reduce the primary precipitate, ferrihydrite, to magnetite (Dauphas and Kasting, 2011; Reinhard and Planavsky, 2011). If organic matter were limiting, the pCO_2 constraint vanishes. In addition, Rosing et al. (2010) calculated above-zero surface temperature using a combination of 900 ppmv of carbon dioxide, 900 ppmv of methane, and a somewhat lower-than-present planetary albedo. However, such a high CH4/CO2 ratio implies that thick organic hazes should form in the stratosphere (Trainer et al., 2006) and the surface should have been cooled. Thus, it is unclear whether the carbon dioxide concentration in the Archean atmosphere could have been as low as that proposed by Rosing et al. (2010)

The 100-PAL pCO_2 constraint from Rye et al. (1995) is based on analysis of paleosols and is also subject to uncertainty (Sheldon, 2006). Indeed, Sheldon argued that if updated thermodynamic data were used, the approach in Rye et al. (1995) would yield a pCO_2 value lower than 1 PAL. These geological constraints, weak as they are, are for the late Archean and may or may not apply for the early Archean, prior to 3 Ga. Thus, in this work we examine CO_2 concentrations between 10 and 100 PAL, recognizing that still higher pCO_2 values cannot be ruled out if the paleoarchean was as hot as some researchers have suggested (Knauth and Lowe, 2003).

Predicted atmospheric CH_4 concentrations in the distant past range from ~0.5 ppmv for the prebiotic Earth (Kasting, 2005) to as much as several thousand ppmv for the postbiotic Archean Earth (Kharecha et al., 2005). The estimate for prebiotic CH_4 should probably be revised upward by a factor of 10, based on new measurements of CH_4 emanating from the Lost City hydrothermal ventfield (Kelley et al., 2005; Segura et al., 2007). Even this revised estimate may be too low if serpentinization of seafloor was more common in the past, as some authors have suggested (Martin et al., 2008). After methanogens appeared, the biosphere would have been efficient at converting atmospheric hydrogen into methane, and CH_4 concentrations of hundreds to thousands of ppmv are expected.

H_2 is also important on the early Earth because, along with CH_4, it determines the basic redox state of the atmosphere. The mixing ratio of hydrogen in Earth's early atmosphere should have been around 1000 ppmv if hydrogen escape was limited by diffusion (Kasting, 1993; Tian et al., 2005). If the hydrogen escape from early Earth was energy-limited, H_2 concentrations of the order of 10% could have been possible (Tian et al., 2005), and the methane concentration could have been significantly higher than assumed here. To demonstrate the possibility of efficient HCN formation in Earth's early atmosphere, we focus on the 1000 ppmv CH_4 cases, which are applicable to the post-biotic Earth.

3. Model description

In this work we use a stand-alone photochemical model, updated from the 1-D model of Domagal-Goldman et al. (2008), which is itself a derivative of the model of Pavlov et al. (2001). A major improvement of the present model is the inclusion of HCN and its relevant chemical species in the species list (Tables 1 and 2), and the addition of HCN-relevant chemical reactions in the reaction list (Supplemental Material). The model now includes 48 long-lived species (for which transport is considered) and 30 short-lived species (assumed to be in photochemical equilibrium), linked by 434 chemical reactions.

Most long-lived species are assigned deposition velocities at the lower boundary similar to those in Domagal-Goldman et al. (2008), based on their solubility and potential to react with surface materials. The temperature profile used in the model is shown in Fig. 1. The water vapor content in the troposphere is controlled by the temperature profile. Above the tropopause water vapor is calculated by solving the combined equations of photochemistry and transport. Both the temperature and the water vapor profiles used in the model are shown in Fig. 1. For the added HCN-relevant species, we choose high deposition velocities of the order of 1 cm/s for HNCO, NCO, and CN. Simulations show that the chemical sources and sinks of these species are in good balance and thus the deposition velocities do not affect the model results. A low deposition velocity of 7×10^{-3} cm/s is used for weakly soluble HCN (Henry's Law constant $k°_H = 7.5$ mol/kg bar according to the NIST database), following Zahnle (1986) Sensitivity tests show that although the HCN mixing ratio near the surface is reduced by using higher deposition velocity, the HCN surface deposition flux remains the same, similar to the results in Zahnle (1986) The mixing ratios of CO_2 and CH_4 are fixed at the lower boundary as tunable

Table 1
List of 48 long-lived species.

O	O_2	H_2O	H	OH	HO_2	H_2O_2	H_2	CO	HCO
H_2CO	CH_4	CH_3	C_2H_6	NO	NO_2	HNO	H_2S	HS	S
SO	SO_2	H_2SO_4	HSO	S_2	NH_3	NH_2	N_2H_3	N_2H_4	CH_2^3
C_2H_5	C_2H_2	C_2H_4	C_3H_8	C_2H_3	C_3H_6	C_3H_2	CH_2CCH_2	CH_3C_2H	
N	Glyoxal	HCN	HNCO	NCO	CN	SO_4AER	S_8AER	HCAER	