Formation of hydrogen cyanide HCN under limited discharge conditions in non-reduced ambient air

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The formation of organic compounds in an atmospheric pressure DC corona discharge was examined using a mass spectrometer. Prebiotic organic compounds such as HCN, HCHO, $CH_2(OH)COOH$ originating from non-reduced ambient air were detected as negative ions. Those ion abundances changed by varying the electron knietic energy over the range of 0 to 120 eV. The HCN^- ion was dominantly formed at the lower energy ranges below 12 eV. The abundance of HCN^- decreased gradually with higher energy above 12 eV as those of CHO^- and $CH_2(OH)COO^-$ simultaneously increased.

Hydrogen cyanide HCN formed in electric discharges as a prebiotic organic compound is one of the most interesting topics in plasma chemistry regarding the origin of life. Miller and Urey have found in 1950s that discharges acting on reduced atmospheres, consisting mainly of H_2, CH_4, NH_3 and H_2O, bring about the abundant production of HCN and resulting formation of several biomolecules such as amino acids and nucleobases [1,2]. Since their experiments, numerous studies to investigate the formation mechanism of organic compounds in discharges have been performed using various gas mixtures involving not only reduced but also neutral atmospheres such as CO_2, CO and N_2, which correspond to the primitive atmosphere's compositions. Those previous studies have shown that the formation of biomolecules by the action of discharges on neutral gas mixtures is much *less* efficient than when reduced atmospheres are used, because of *less* production of prebiotic HCN in neutral gases [3], leading to the discussion to reassess whether the HCN was involved in the origin of life or not. Here we examined the species and abundances of organic compounds generated in an atmospheric pressure DC corona discharge with electron kinetic energies over the range of 0 to 120 eV using a mass spectrometer, and found the limited energy ranges which result in the dominant formation of the HCN even in non-reduced ambient air.

Discharge experiments were performed under atmospheric pressure in laboratory air, which mainly consists of common air constituents such as N_2, O_2, H_2O and CO_2, with relative humidity of 70 % at 298 K. The tip of the corona needle used had a radius of ca. 1 μm, and the shape of the tip surface was adequately approximated by a hyperboloid of revolution (Figure 1a). The opposite electrode was the stainless steel orifice plate of the mass spectrometer (JMS LCmate, JEOL, Japan). The formation of various ionic and neutral species in atmospheric pressure corona discharges is attributed to kinetic energy *KE* of electrons acclerated on the needle tip surface with a given electric field strength *E* (*KE* = $E \times \lambda_e$; λ_e corresponds to the mean free path of electron, 375 nm in ambient air). It has been previously found that the field strength *E* and resulting electron energy *KE* in the discharge system

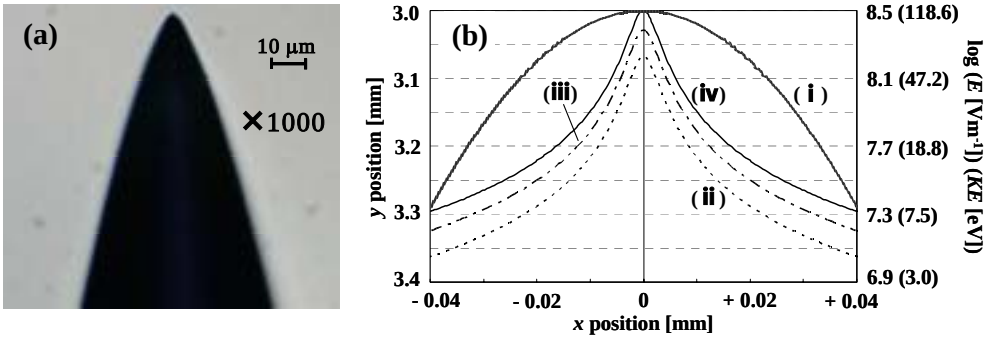
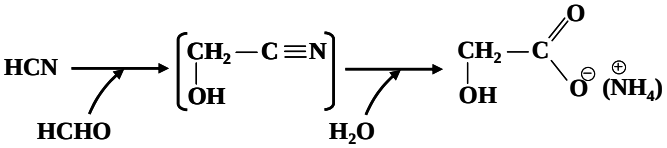


Fig. 1: (a) Optical micrograph of the needle tip. (b- i) The hyperbola representing the contour of the cross-sectional needle tip and the calculated electric field strength distributions on the needle tip as a function of *x* coordinate of the tip for three potential differences (ii) 1.9, (iii) 2.7 and (iv) 3.5 kV.

used here are determined by the DC corona voltage and the local curvature of each needle tip position [4]. Figure 1b shows the calculated field strength distributions on the needle tip for three potenetial differences (1.9, 2.7 and 3.5 kV) under the discharge gap of 3 mm as a function of x coordinate of the needle tip. The tip apex with the highest curvatures (x = 0 in Figure 1b) brings about particularly high field strength above 10^8 Vm^{-1} at any corona voltages, leading to the generation of electrons with high kinetic energy over the range of 60 to 120 eV. In the case of the tip peripheral region with lower curvature ($|x|$ > 0.02 mm in Figure 1b), in contrast, a variety of corona voltage results in the production of the electrons with various kinetic energies from 0 to 10 eV. Therefore, the use of various combinations of the corona voltage and local curvatures makes it possible to accurately regulate the electron kinetic energy over the range of 0 – 120 eV in this discharge system.

The ionic species related to HCN were detected in negative corona, while in the case of positive corona, the oxonium ion H_3O^+ was dominantly formed under any discharge conditions. Figure 2a shows the mass spectrum including the dominant peak of the HCN^- ion at m/z 27 formed by the electrons with kinetic energy of 64 eV, which originated from the corona voltage of -1.9 kV and tip local curvature at x = 0 in Figure 2b. This mass spectrum, furthermore, contained the other prebiotic organic ions, such as the deprotonated ions of formaldehyde CHO^- at m/z 29 and glycoric acid $CH_2(OH)COO^-$ at m/z 75, as well as various inorganic ions, e.g., HO^- at m/z 17, CO^- at m/z 28, CO_2^- at m/z 44, NO_2^- at m/z 46, HCO_3^- at m/z 61 and NO_3^- at m/z 62. The abundances of the prebiotic organic ions HCN^-, CHO^- and $CH_2(OH)COO^-$ considerably changed with varying the electron kinetic energy KE over the range of 0 to 120 eV, as shown in Figure 2b. The HCN^- ion was dominant at the lower energy ranges below about 12 eV ($\log E \approx 7.5$) with maximum in abundance at 12 eV, and its abundance gradually decreased at higher energies above 12 eV. Instead, CHO^- and $CH_2(OH)COO^-$ appeared at 12 eV and increased continuously up to the highest energy. It has been known that HCN can form $CH_2(OH)COOH$ via the Strecker synthesis involving HCHO as follows [5]:



(1)

It is most likely, therefore, that the decrease in abundance of HCN^- at higher energy ranges above 12 eV is attributed to the production of HCHO and simultaneous promotion of reaction (1). These results suggest that the progress of the reactions to form the prebiotic organic compounds considerably changes with varying the electron energy, and that HCN can be dominantly formed at the limited energy range (≤ 12 eV) even in non-reduced ambient air.

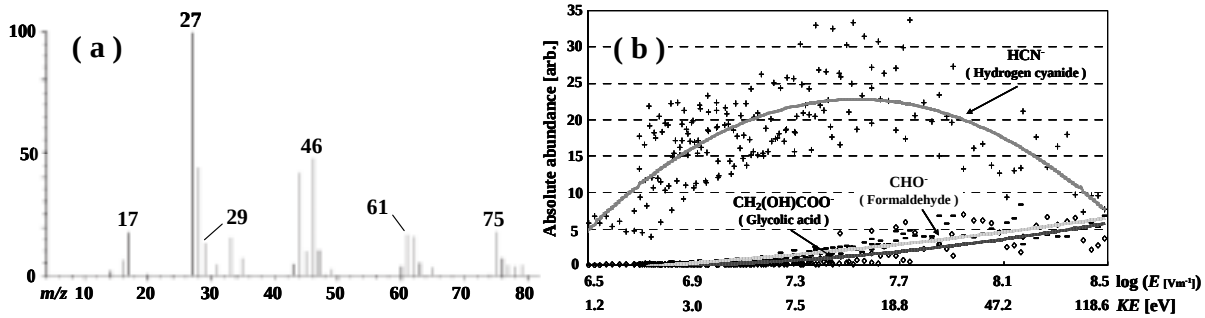


Fig. 2: (a) Negative ion corona dsicharge mass spectrum of ambient air with electron kientic ennergy of 64 eV. (b) Influence of absolute abundances of the prebiotic organic ions on the electric field strength on the needle tip E and resulting electron kinetic energy KE.

References

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