STUDY ON THE PHOTOCHEMICAL REACTION OF HCN AND ITS POLYMER PRODUCTS RELATING TO PRIMARY CHEMICAL EVOLUTION

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Abstract. The photochemical reaction of HCN at 184.9 nm is studied in the gas phase. $(CN)_2$, H_2, CH_4, NH_3, N_2H_4, C_2H_6, and CH_3NH_2 are identified as gas phase products, and a reaction mechanism is proposed. HCN polymers** are also obtained as solid reaction products, and their structure is investigated by Infrared Spectroscopy, UV-Visible Spectroscopy, Mass Spectrometry, and Amino Acid Analysis. The process and nature of the formation of the polymers are discussed.

1. Introduction

The chemistry of HCN is drawing increasing attention because of its importance in the abiogenetical synthesis of organic compounds as well as in industrial syntheses. As early as the 19th century, polymerization reactions of liquid HCN by the addition of a small amount of several bases were reported. The formation of azulmic acid from a mixture of HCN, NH_3, and H_2O was also reported. Lange (1873) and Wippermann (1874) found glycine in the hydrolyzates of HCN polymers. The polymerization reactions of HCN in the gas phase by α-particles (Lind *et al.*, 1926) or UV irradiation (Villars, 1930) were early studies in this field.

Gradual progress in cyano-carbon chemistry began when Miller (1957) reported that HCN is a precursor of several amino acids when a mixture of H_2, CH_4, NH_3, and H_2O is subjected to electric discharge. Since then the importance of HCN as a key compound in the chemical evolutionary process has been claimed by many in-

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** The solid phase product of HCN obtained by the UV irradiation is referred to as 'HCN polymers' in this paper. Neither the exact composition nor the structures of the components have yet been determined. The authors would like to remind the reader that the degree of polymerization may be small enough for some of the components so that it may be improper to call them polymers in a strict sense, and we have used the word in a broad sense for convenience.

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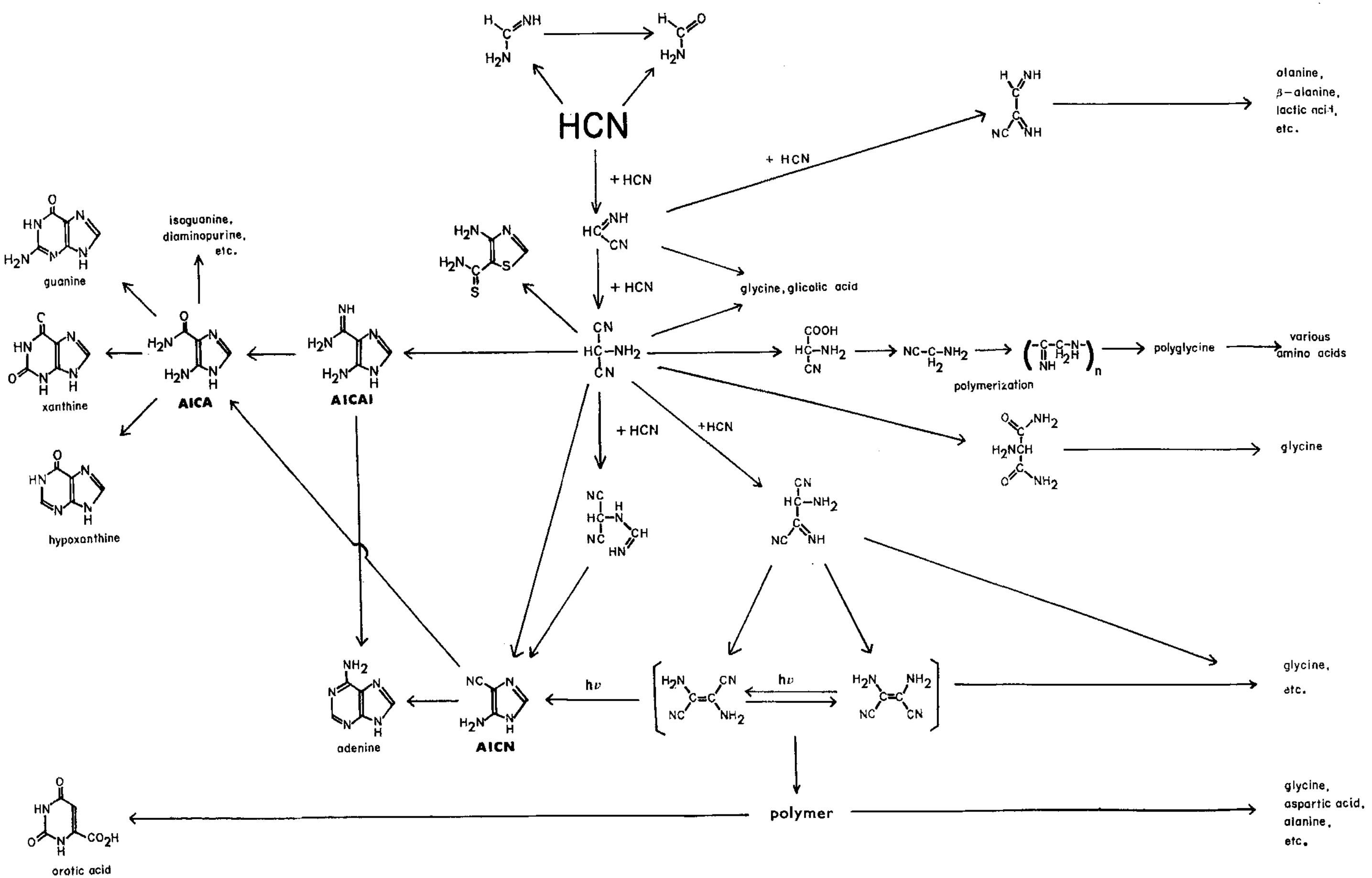

Fig. 1. Summarized reaction pathways from HCN to bio-organic molecules, so far proposed by many investigators.

vestigators (Ferris *et al.*, 1973, and references therein). The partial structure of the HCN polymers was proposed by Ruske and Ruske (1958) and Völker (1960), although this is not yet fully confirmed. The processes of polymerization were also investigated, and the structure of the tetramer of HCN was determined by Penfold and Lipscomb (1960) and Long *et al.* (1960). That of the trimer was elucidated by Ferris and Orgel (1965). The structure of the dimer was first proposed by Moser *et al.* (1967). The proposed structure was shown to have the lowest energy among the isomers examined (Jameson and Yang, 1972), however, a complete picture of the dimer, an intermediate in the polymerization reaction, is yet to be elucidated.

In experiments simulating the conditions on the primitive Earth, the formation of a number of organic molecules from HCN has been reported by several authors. Oró and Kimball (1961) reported the formation of adenine and other purine intermediates. Amino acids are also known to be formed when HCN is passed through aqueous ammonia (Oró and Kamat, 1961). Figure 1 summarizes the results of these studies (for original references to individual experiments, cf. Sanchez *et al.*, 1967; Ferris *et al.*, 1973; etc.).

Though Villars (1930) found that the irradiation of HCN with a hydrogen discharge lamp gives H_2 and a polymeric substance of the composition $(CN)_x$, no quantitative study of the photochemical reaction of HCN in gas phase has been published apart from our preliminary reports (e.g., Mizutani *et al.*, 1972). Since UV irradiation is considered to be the most abundant energy source on the primitive Earth (Calvin, 1969), the irradiation of HCN by 184.9 nm light is of interest to those studying chemical evolution as well as ultraviolet photochemistry.

2. Experimental

2.1. APPARATUS

A low-pressure mercury lamp was used as the light source. The electrodes of the lamp were cooled by a water jacket to keep the temperature of the lamp constant at 47 °C. The UV light emitted from the lamp is mostly composed of two resonance lines, namely 184.9 nm and 253.7 nm. Since HCN only absorbs 184.9 nm light, no filter was used to eliminate 253.7 nm light. Further, we confirmed that 253.7 nm light does not affect the nature of the gaseous products (Mizutani, 1973).As will be described later, however, it was found that 253.7 nm light is involved in the secondary reaction of the polymers which can absorb it. The total light input to the reaction cell at 184.9 nm was measured by N_2O actinometry in each irradiation experiment (Calvert and Pitts, 1967), and was initially about 5.6×10^{16} quanta s^{-1}. The amount of absorbed light in each experiment tended to decrease with the increase of the amount of polymer deposit on the wall of the reaction cell.

A reaction cell of the two-chambers-jointed-type was used. The inner diameter of the cell was 5 cm, and the volumes of two chambers were 114 cc each. One chamber was for the reaction of HCN and the other for the measurement of the amount of absorbed light. Since the extinction coefficient of HCN at 184.9 nm was not known, measurement of the coefficient was made according to the method described elsewhere (Mizutani, 1973), and gave 0.51 cm^{-1} atm^{-1} as an approximate value of the coefficient. A detailed description of the method for determining the number of absorbed quanta is in the reference mentioned above. Both the mercury lamp and the reaction cell were covered by a glass cylinder, and air in the cylinder was replaced by nitrogen during experiments in order to eliminate the absorption of 184.9 nm light by oxygen. The evacuation system consisted of a rotary pump and an oil diffusion pump; the lowest attainable pressure of the system was lower than 10^{-5} torr. Throughout the experiments, a liquid N_2 trap was used to prevent possible contamination by mercury. Contamination could only have occurred during the collection of gaseous products. In addition, a gold foil was placed in the trap to prevent the diffusion of trapped mercury while the apparatus was at rest.

2.2. MATERIAL

HCN was synthesized by means of the acidification of KCN with H_2SO_4. Crude HCN was led into a vacuum system and purified by distillation. The purity of HCN was higher than 99.96%, and the detectable impurity by gas liquid chromatography was cyanogen.

Cyanogen for use as a gas chromatographic standard was obtained by the pyrolysis of AgCN, and its purity was higher than 99.9%.

CH_4, C_2H_6, H_2, and N_2 were purchased from Takachiho Kogyo Co.,Ltd. and used as gas chromatographic standards without further purification. N_2O and NO were also purchased from the same manufacturer and distilled in a vacuum system before use. N_2O was used for actinometry, and NO was used as a radical scavenger.

2.3. ANALYSIS

The method of analysis of the reaction products is described elsewhere in detail (Mizutani, 1973).

The identification of gaseous reaction products and the determination of their yields were mainly carried out by gas chromatography. Several spot tests and mass spectrometry were also applied for further confirmation. A Shimadzu GC 4APTF Gas Chromatograph was used, and the conditions for the analyses were as follows: For HCN and $(CN)_2$; Column, stainless 2 m long and 3 mm inside diameter. Packing, triacetin 25 wt% chromosorb P NAW 30–60 mesh. Carrier gas, He. Temperature, 45 °C. Inlet pressure, 0.8 kg cm^{-2}. Flow rate, 40.7 cc min^{-1}. For H_2 and hydrocarbons; Column, stainless 4 m long and 3 mm inside diameter. Packing, active alumina (T.R.) 30–60 mesh. Carrier gas, N_2. Temperature, 50 °C. Inlet pressure, 1.2 kg cm^{-2}. Flow rate, 11.7 cc min^{-1}. Under these conditions, the retention time of HCN was 57.5 s and that of $(CN)_2$ was 42.5 s.

For the study of solid products, or HCN polymers, IR, UV-visible spectrophotometry, and mass spectrometry were combined. Hitachi IR spectrophotometers EPI-G2 and EPI-G3, an automatic UV-visible spectrophotometer EPS-2, and a mass spectrometer RMU-6 were uses. In the case of the IR study, polymers were extracted by solvents and mixed with KBr powder. The mixtures were put under vacuum ($<10^{-1}$ torr) overnight at room temperature. About 1 mm thick KBr discs of 10 mm diameter were prepared from thus dried powder. A disc made according to the above procedure but using only solvents rather than polymer solution was used as a reference. For MS study, solvent-extracted polymers were put under vacuum ($<10^{-2}$ torr) at room temperature for 10 minutes after all the solvent had evaporated. The dried sample was then directly introduced into the mass spectrometer. An automatic amino acid analyzer was used for analysis of HCl hydrolyzates of HCN polymers. Conditions for the hydrolysis are included in Table II. Paper chromatography with several different solvents was also used for the analysis of HCN polymers and their hydrolyzates. The presence of glycine in the hydrolyzates was confirmed by paper chromatography with two different solvents in addition to the retention time on the amino acid analyzer.

3. Results

3.1. GAS PHASE PRODUCTS

The major products in the gas phase are $(CN)_2$ and H_2, and minor products are CH_4, C_2H_6, NH_3, N_2H_4, and CH_3NH_2. N_2 and C_2H_4 are not detected. The quantum

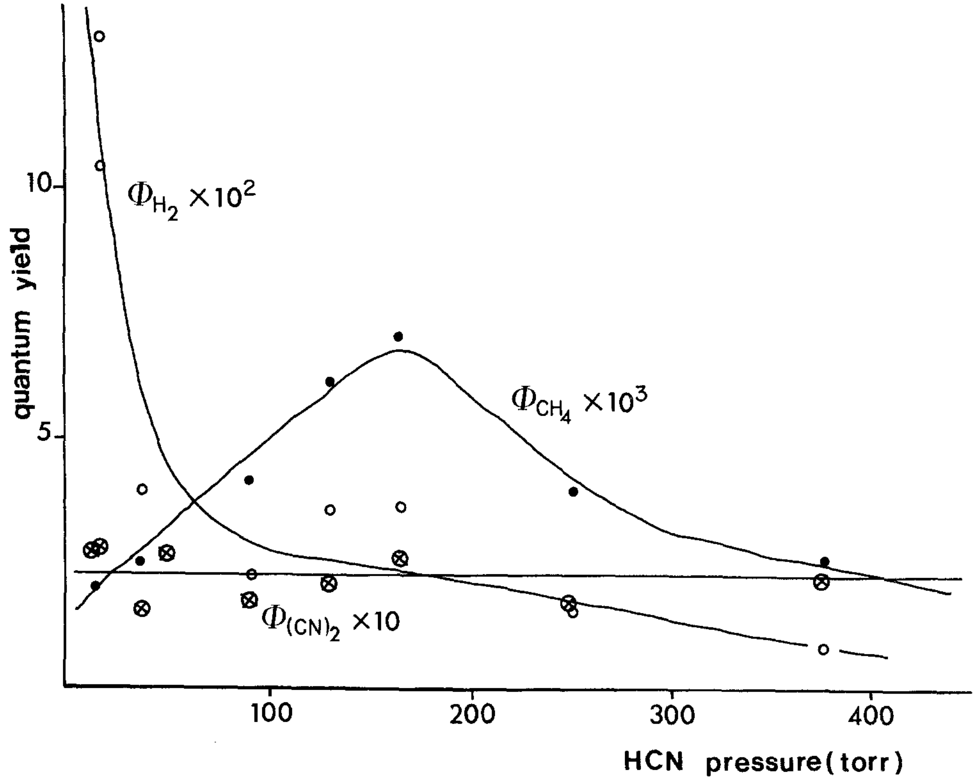

Fig. 2. Dependence of the quantum yields of H_2, $(CN)_2$, and CH_4 on initial HCN pressure.

yields of minor products are, $\Phi_{C_2H_6}=1\times10^{-4}$ at 49 torr of HCN, $\Phi_{NH_3}>2\times10^{-3}$ at 59 torr of HCN, $\Phi_{N_2H_4}>5\times10^{-6}$ and $\Phi_{CH_3NH_2}=1\times10^{-4}$ at 72 torr of HCN.

The dependence of the quantum yields of H_2, $(CN)_2$, and CH_4 on the initial pressure of HCN is shown in Figure 2. The quantum yield of $(CN)_2$ is independent of the pressure of HCN. The quantum yield of H_2 decreases with the increase of HCN pressure, indicating the addition of atomic hydrogen to HCN. The effect of the addition of a small quantity of NO as a radical scavenger into the reaction system was also investigated. The quantum yields of H_2 showed an average decrease of 92% by the addition of about 7% NO, and the yield of CH_4 was reduced to 1%, when less than 4% of NO was added to HCN. The results suggest that the H atom and the methyl radical are involved in the formation of H_2 and CH_4. On the other hand, the yield of $(CN)_2$ is not affected by the addition of a small amount of NO. The reason may be that cyanogen radicals are not scavenged by NO.

Considering these results, we may assume that the primary step of the reaction is the formation of a H atom and a CN radical (either $A^2\Pi$ or $X^2\Sigma^+$). The photolysis of HCN to form gaseous products may be represented as follows:

$$HCN\xrightarrow{h\nu}\cdot H+\cdot CN \tag{1}$$

$$\cdot H+\cdot H\xrightarrow{M}H_2 \tag{2}$$

$$\cdot CN+\cdot CN\xrightarrow{M}(CN)_2 \tag{3}$$

$$\cdot H+HCN\rightarrow H_2CN\ \text{(radical)} \tag{4}$$

$$\cdot H+H_2CN\rightarrow(H_2C{=}NH) \tag{5}$$

$$\cdot H+(H_2C{=}NH)\rightarrow H_4CN\ \text{(radical)} \tag{6}$$

$$\cdot H+H_4CN\rightarrow\cdot CH_3+\cdot NH_2 \tag{7}$$

$$\cdot H+\cdot CH_3\xrightarrow{M}CH_4 \tag{8}$$

$$\cdot H+\cdot NH_2\xrightarrow{M}NH_3 \tag{9}$$

$$\cdot CH_3+\cdot CH_3\xrightarrow{M}C_2H_6 \tag{10}$$

$$\cdot NH_2+\cdot NH_2\xrightarrow{M}N_2H_4 \tag{11}$$

$$\cdot CH_3+\cdot NH_2\xrightarrow{M}CH_3NH_2 \tag{12}$$

M denotes a third body, which absorbs excess energy generated by a recombination of two atom(s) and/or radical(s).

Though we could not confirm the production of $H_2C{=}NH$ (methyleneimine), its formation has been observed in the reaction of atomic hydrogen with HCN at 77 K (Sherwood and Turner, 1971). In addition, it was detected by means of a mass spectrometer with molecular beam sampling, when the mixture of CH_4 and NH_3 was subjected to an electrodeless microwave discharge (Herbrechtsmeier and Wagner, 1971). $H_2C{=}NH$ might not be stable enough at room temperature to be detected by the methods we employed (Johnson and Lovas, 1972). Furthermore, the abundant existence of H atoms in the reaction system is also unfavorable to the survival of $H_2C{=}NH$, causing the successive reactions (6) and (7).

This mechanism can explain qualitatively the dependence of the products, H_2 and $(CN)_2$, on HCN pressure. The behavior of Φ_{CH_4} showing a maximum at *ca.* 160 torr of HCN is not well understood at present, since the concentration of methyl radicals would be expected to increase with an increase in the pressure of HCN. A probable explanation may be the removal of methyl radicals due to their addition to HCN to start the polymerization of HCN. It is observed that the formation of HCN polymers becomes rapid at higher pressures of HCN.

3.2. SOLID PRODUCTS

After a few hours of irradiation, a reddish brown substance (HCN polymers) adherent to the surface of the reaction cell becomes noticeable. The electronic absorption spectrum of the polymers is structureless, and the absorbance decreases monotonously towards the IR region. The analysis of the dependence of the absorption spectrum on the irradiation time revealed that a UV absorbing substance(s) appears first and its absorption region gradually extends to the visible region with prolonged irradiation, indicating that the colored substance is not the primary product of the reaction, while the UV absorbing substance is directly related to the primary reaction process (Noda *et al.*, 1975). When NO is introduced into the reaction cell, the rate of formation of the colored substance becomes negligible. The UV absorbing substance is, however, still formed in the presence of NO, suggesting that the formation of the colored substance depends on some secondary processes.

The effect of 253.7 nm light irradiation upon these processes was examined. Table I shows the relative increase of optical densities of the polymers at various wavelengths. The initial amounts of the polymer deposits on the reaction chamber in two experiments, i.e., with and without 184.9 nm light, were chosen so that they were nearly

TABLE I
The effect of 253.7 nm light on the formation of colored substance

Wavelength (nm)	Increase of optical density		$O.D._{253.7}$–$O.D._{184.9}$
	184.9 nm	Only 253.7 nm	
220	0.106	0.069	0.65
310	0.077	0.040	0.52
440	0.052	0.073	1.4
500	0.043	0.071	1.7
700	0.025	0.037	1.5

Initial HCN pressures are 115 torr for 184.9 nm irradiation and 113 torr for only 253.7 nm irradiation. Irradiation time for the former experiment was 10 min and for the latter, 60 min. Initial optical densities are as follows: For 184.9 nm experiment; 0.669 at 220 nm, 0.465 at 310 nm, 0.258 at 440 nm, 0.189 at 500 nm, and 0.082 at 700 nm. For only 253.7 nm experiment; 0.616, 0.481, 0.258, 0.187, and 0.071 respectively.

equal to each other. The initial HCN pressures were also chosen to be nearly equal. Since 184.9 nm light is far more effective in producing HCN polymers, the irradiation times were different in these two experiments so that comparable increases in optical densities are attained. Since HCN does not absorb 253.7 nm light, these results indicate the existence of a secondary reaction starting from the absorption of ultraviolet light by the polymers. This secondary reaction seems to favor the formation of colored substances over colorless one.

The solid products were separated by solvent extractions into several fractions. The CH_3OH soluble fraction of the polymers had a similar IR spectrum to that of the product obtained in a CH_4, NH_3 discharge experiment (experimental detail of the discharge unpublished; cf. Mizutani, 1972), indicating the existence of $=N-H$, $-C\equiv N$ (conjugated), $-N-H$, $-NH_2$, and $-C-H$ bonds. The IR spectrum of the dimethyl sulfoxide (DMSO) soluble fraction was slightly different but similar (Mizutani and Noda, 1972).

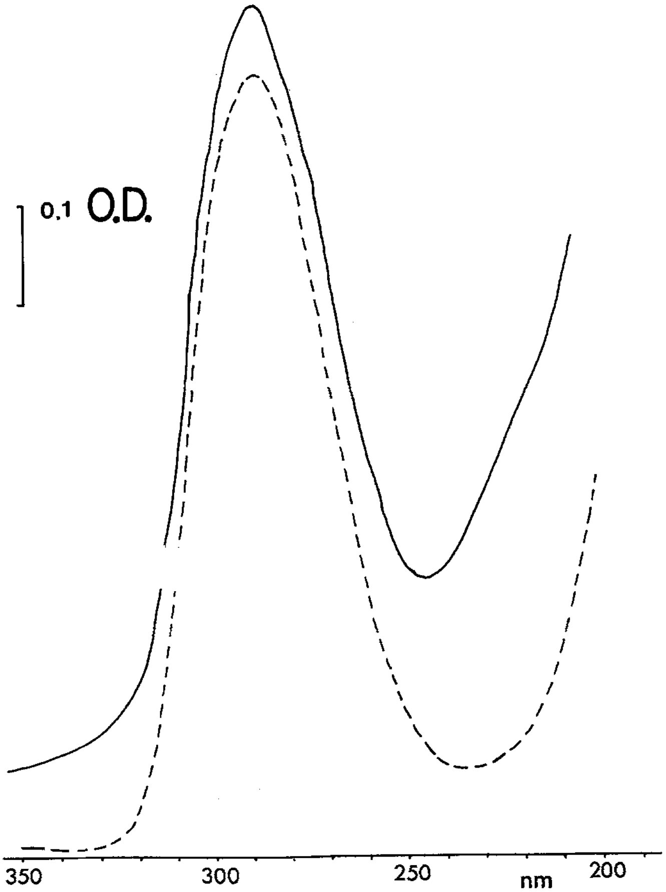

Fig. 3. UV spectra of the ethyl ether soluble fraction of HCN polymers (solid line) and the ethyl ether solution of DAMN (broken line).

The ethyl ether soluble fraction, which constitutes a small part of the polymers, shows quite similar features in the UV absorption spectrum to that of ethyl ether solution of HCN tetramer (diaminomaleonitrile = DAMN) as shown in Figure 3.

Mass spectra of the CH_3OH soluble fraction and DAMN are shown in Figure 4.

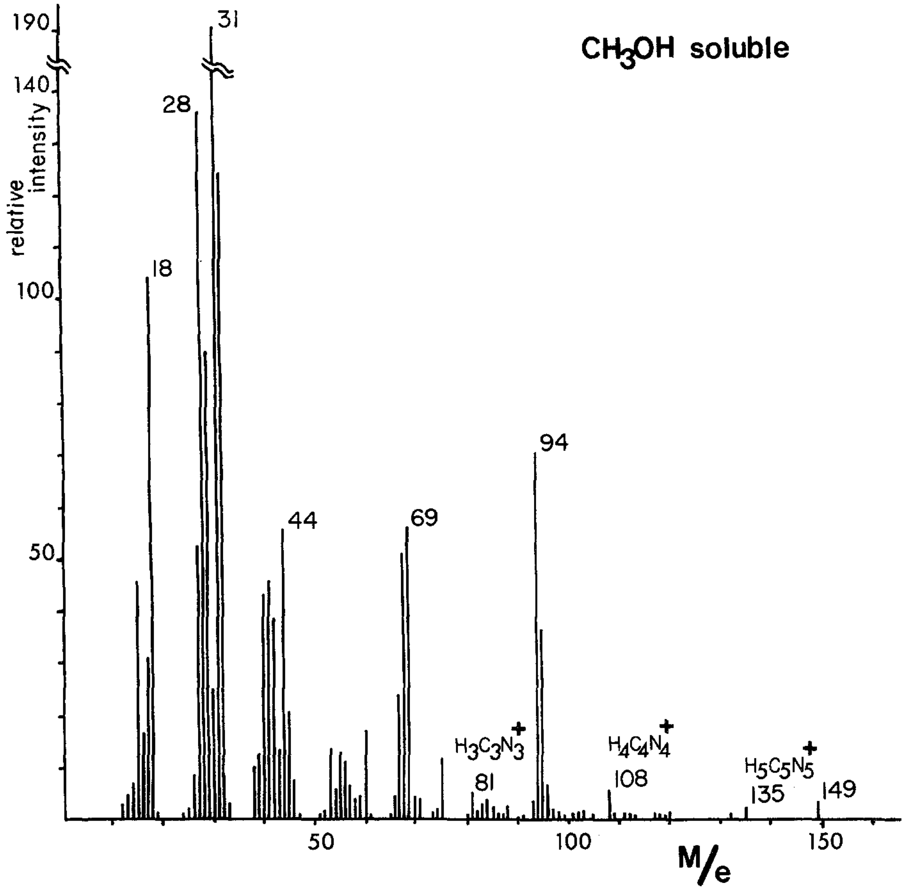

Fig. 4a.

Fig. 4. Mass spectra of the CH_3OH soluble fraction of HCN polymers and DAMN.

The prominent peaks of DAMN appear at $M/e = 28$ (H_2CN^+), 54($H_2C_2N_2^+$), 81($H_3C_3N_3^+$), and 108($H_4C_4N_4^+$). These peaks are also observed in the case of the CH_3OH soluble fraction, but more intense peaks are found midway between the peaks of these HCN oligomers, i.e., $M/e = 94$ (probable formula would be $C_4H_4N_3^+$), 69 (probable formula $C_3H_5N_2^+$), 44 ($CH_4N_2^+$ and/or $C_2H_6N^+$). The CH_3OH soluble fraction seems to begin decomposing at above 150 °C, while DAMN decomposes at 182–184 °C.

Amino acid analysis was applied to the acid hydrolyzates of solvent extractions of the polymers. Table II shows the results as well as those of the analysis of known HCN oligomers (DAMN and adenine) and the CH_3OH soluble fraction of the CH_4, NH_3 discharge products. The yields of glycine and NH_3 decrease in the order of tetramer (DAMN), pentamer (adenine), CH_3OH soluble, DMSO soluble. The number of the minor products detected only in trace amounts increases in the same order. Therefore, this order may reflect not only increasing molecular weight but also the increasing complexity of structures of these HCN polymers. The CH_4, NH_3 discharge product gave more diverse amino acids of significant amounts, although the yield of glycine is greater than in the DMSO soluble fraction. This may suggest comparative or slightly more complicated structures for the discharge product.

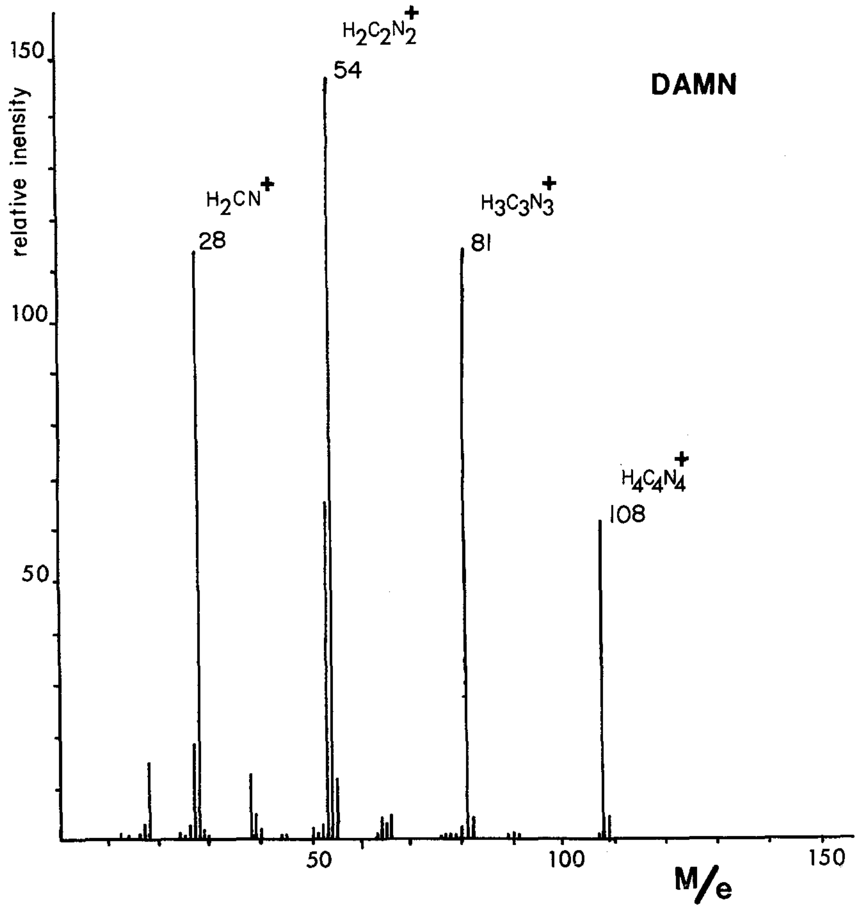

Fig. 4b.

TABLE II

Amino acid analyses of the hydrolyzates of HCN polymers[a]

Products	Diamino-maleonitrile	Adenine	HCN photolysis		CH_4, NH_3 discharge
			Methanol soluble	DMSO soluble	Methanol soluble
NH_3	18	7.2	3.2	0.85	nd
Gly	6.1	3.2	0.62	0.33	0.41
Glu	0	0	+	+	0.06
Ala	0	0	+	0	0.05
Asp	0	0	+	+	0.02
His	0	+	+	+	+
Arg	0	0	0	+	0.01
Lys	0	0	+	0	+
Ser	0	0	0	+	+
Thr	0	0	0	+	+
Val	0	0	0	+	+
Ile	0	0	0	+	+
Leu	0	0	0	+	+

The unit of the figures is μmole (mg polymer)$^{-1}$, and + indicates formation of amino acid, but its amount is less than 0.005 μmole (mg polymer)$^{-1}$. The conditions of hydrolysis are: 6N HCl, 24 hr, 109 °C for DMSO- and methanol-soluble fractions of HCN photolysis products, and adenine; 6N HCl, 24 hr, 102 °C for diaminomaleonitrile; 6N HCl, 20 hr, 110 °C for methanol-soluble fraction of CH_4–NH_3 discharge products. nd = not determined.

[a] The assignments of amino acids are tentative except in the case of glycine. Especially Glu and citrulline have nearly identical retention times so that they are indistinguishable.

4. Discussion

Though the nature of the atmosphere on the primitive Earth is not yet fully known (Holland, 1962; Abelson, 1966), it may be reasonable to assume the existence of HCN in the primitive atmosphere, since the formation of HCN is quite commonly observed when a mixture of simple carbon-containing compound(s) (for instance CH_4, CO, C_2H_2, C_2H_4, C_2H_6) and nitrogen-containing compound(s) (for instance N_2, NH_3) is subjected to various chemically activating treatments (e.g. heat, shock tube heating, electric discharge, electron bombardment, γ-ray irradiation). Miller's famous discharge experiment of CH_4, NH_3, H_2O, H_2 mixtures revealed the formation of amino acids, but the reaction conditions in these types of experiments were too complicated to establish the most important processes in forming purine bases or amino acids which were identified as the reaction products. Our present study confirms the importance of gaseous HCN as well as liquid or aqueous HCN in forming HCN polymers which will give amino acids after hydrolysis. Also we would like to point out the greater importance of UV irradiation compared with electric discharge as an energy source in chemical evolution.

Among various volatile compounds identified by our present study, the formation of simple basic substances (NH_3, $H_2C{=}NH$, and CH_3NH_2) is quite interesting. It has been known that HCN and $H_2C{=}NH$ exist in interstellar space (IAU Circular

No. 2251, 1970 and No. 2410, 1972, respectively), and the formation of $H_2C=NH$ might be due to the addition reactions of H atom to HCN (Iguchi *et al.*, 1973). The existence of CH_3NH_2 in the interstellar space had been predicted (Iguchi *et al.*, 1973), and quite recently was discovered in Sagittarius B and in the Orion nebula (Kaifu *et al.*, 1974). Although the detailed mechanism of HCN polymerization is still ambiguous, it is well known that basic substances catalyze the polymerization of HCN in liquid or aqueous solution (Matthews and Moser, 1967; Koenig, 1969; Kurabayashi *et al.*, 1969). In our experiments, the polymer formation still proceeded after the termination of irradiation unless gaseous products were taken out from the reaction cell, indicating that the base catalyzed polymerization of HCN was going on to some extent in the dark. That is to say, the photolysis of HCN itself can make catalysts, bases, for polymerization, even though there were no bases initially. In this way, a good number of HCN molecules in the primitive atmosphere might have polymerized.

The polymers obtained in the photochemical decomposition of HCN are a mixture of various molecular weights, and they can be separated into several fractions by solvent extraction, though it appears to cause some secondary changes of the products (Mizutani *et al.*, 1974). Further separation of CH_3OH soluble fraction was done using Shimadzu Dupont LC-830 Liquid Chromatograph. As a tentative result, a poly-styrene gel column with THF (tetrahydrofuran) as the mobile phase gave about 6 peaks in the chromatogram, with estimated molecular weights ranging from one hundred to two thousand. It is noteworthy that this molecular weight range just coincides with that of the CH_3OH soluble fraction of CH_4, NH_3 discharge products obtained by means of equilibrium ultracentrifugation (Noda and Ponnamperuma, 1971). The complete separation of these polymer mixtures and the determination of their molecular weights and structures are left for future investigations.

IR spectra of HCN polymers indicate that the structures of HCN photolysis products are related to that of CH_4, NH_3 discharge products. UV spectrum of the ethyl ether extraction fraction of HCN polymers appears similar to that of DAMN, HCN tetramer. Amino acid analysis of the hydrolyzates of polymers shows that NH_3 and glycine are the main products. The existence of various amino acids in minor amounts is also interesting, but further investigation will be necessary to confirm the identification of these minor products, for they were identified only by retention times on the chromatogram unlike the identification of the major product, glycine. It is reported that the identification of amino acids by their retention times is quite unreliable (Ferris *et al.*, 1974).

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