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THE PHOTOCHEMICAL REACTION OF HYDROGEN CYANIDE IN GAS PHASE AT 184.9 nm

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The photochemistry of hydrogen cyanide at 184.9 nm was studied. Major reaction products are cyanogen and hydrogen, and minors are methane, ammonia, ethane, hydrazine and methylamine. The addition of hydrogen atoms to hydrogen cyanide is considered for the formation of these products. A reddish brown polymeric substance was also obtained and its IR spectrum is presented.

The important role of hydrogen cyanide as a precursor in abiogenetical synthesis of organic compounds was proposed by several investigators$^{1)}$. They showed that the polymerization products of hydrogen cyanide, including purine bases, were formed by the ultraviolet irradiation of aqueous solution of hydrogen cyanide. As the solar radiation in the vacuum ultraviolet region might have reached through the primitive atmosphere to the surface of the earth, it would take an important part in the chemical evolution on the primitive earth. The photochemical reaction of hydrogen cyanide in gas phase by vacuum ultraviolet light seems not to have been studied until present. Villars$^{2)}$ found that the irradiation of hydrogen cyanide with hydrogen discharge-lamp gave hydrogen and polymeric substance of the composition of $(CN)_x$. Here we report the study of the photochemical reaction of hydrogen cyanide at 184.9 nm.

A low-pressure mercury lamp was used for light source. The light intensity of the lamp at 184.9 nm was determined by N_2O actinometry, and was estimated to be about 5.6×10^{16} quanta/s. As hydrogen cyanide has no absorption above 191.5 nm, we do not use any filter to exclude 253.7 nm light. The analysis of the reaction products was done by gas chromatography, spot tests and mass spectrometry.

Major products were cyanogen and hydrogen, and minor products were methane, ethane, ammonia, hydrazine and methylamine. Nitrogen and ethylene were not detected. Fig. 1 shows the dependence of the quantum yields of hydrogen, cyanogen and methane on the initial pressure of hydrogen cyanide. The quantum yield of hydrogen decreased with the increase in the pressure of hydrogen cyanide, while those of cyanogen and methane decreased as the pressure of hydrogen cyanide decreased. The quantum yields of minor products are, $\phi_{C_2H_6} = 1 \times 10^{-4}$ at 49 Torr of HCN, $\phi_{NH_3} > 2 \times 10^{-3}$ at 59 Torr of HCN, $\phi_{N_2H_4} > 5 \times 10^{-6}$ and $\phi_{CH_3NH_2} = 1 \times 10^{-4}$ at 72 Torr of HCN.

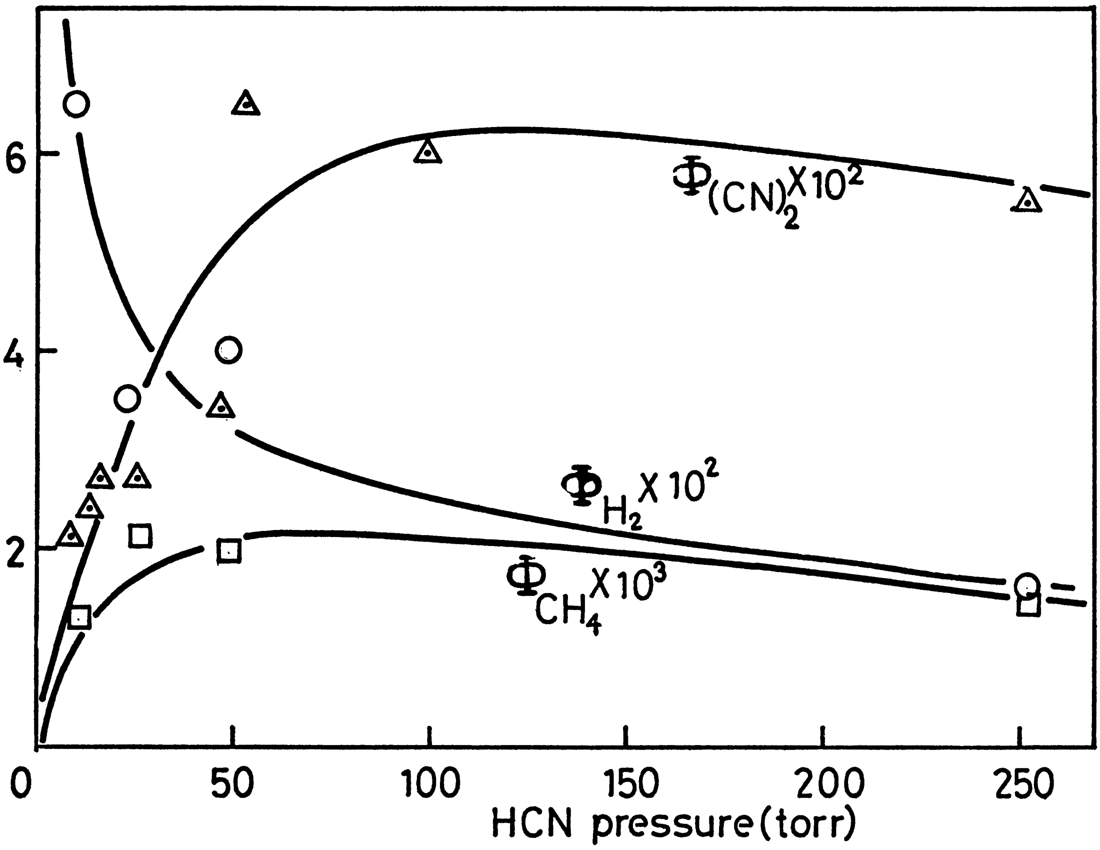

Fig. 1. The dependence of the quantum yields of methane, cyanogen and hydrogen on the initial pressure of hydrogen cyanide.

We presume the primary step in the photolysis of hydrogen cyanide is the formation of hydrogen atom and cyanogen radical although the predissociation of hydrogen cyanide at 184.9 nm (54083 cm^{-1}) is not certain. Herzberg et al.[3 a), b)] estimated the predissociation limit of hydrogen cyanide to be 55260 cm^{-1}, but they noted the possibility that this limit might be much lower, and Okabe et al.[4)] observed the weak emission of cyanogen radical ($A^2\Pi$), irradiating hydrogen cyanide at 184.9 nm. At any rate, these spectroscopic data seem not necessarily to confirm the production of either CN ($A^2\Pi$) or CN ($X^2\Sigma^+$) in a high quantum yield, so that at present the primary step to form hydrogen atom and cyanogen radical may be considered as a tentative one. The decrease of the quantum yield of hydrogen and the increase of that of methane with the increase in pressure of hydrogen cyanide may be interpreted in terms of the multiple addition of hydrogen atoms to hydrogen cyanide. The formation of hydrogen atoms and methyl radicals as intermediate is also confirmed by the remarkable decrease in the production of hydrogen and methane with the addition of NO, as Table 1 shows. The behavior of the quantum yield of cyanogen with the change of the pressure of hydrogen cyanide is not clearly understood at present.

Although the detailed mechanism to form these reaction products may be rather complicated, the main features of photolysis of hydrogen cyanide may be represented as follows.

$\mathrm{HCN} \xrightarrow{h\nu} \cdot\mathrm{H} + \cdot\mathrm{CN}$ (1)

$\cdot\mathrm{H} + \cdot\mathrm{H} \xrightarrow{M} \mathrm{H_2}$ (2)

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

$\cdot\mathrm{H} + \mathrm{HCN} \longrightarrow \mathrm{H_2CN}$(radical) (4)

$\cdot\mathrm{H} + \mathrm{H_2CN} \longrightarrow (\mathrm{H_2C{=}NH})$ (5)

$\cdot\mathrm{H} + (\mathrm{H_2C{=}NH}) \longrightarrow \mathrm{H_4CN}$(radical) (6)

$\cdot\mathrm{H} + \mathrm{H_4CN} \longrightarrow \cdot\mathrm{CH_3} + \cdot\mathrm{NH_2}$ (7)

$\cdot\mathrm{H} + \cdot\mathrm{CH_3} \xrightarrow{M} \mathrm{CH_4}$ (8)

$\cdot\mathrm{H} + \cdot\mathrm{NH_2} \xrightarrow{M} \mathrm{NH_3}$ (9)

$\cdot\mathrm{CH_3} + \cdot\mathrm{CH_3} \xrightarrow{M} \mathrm{C_2H_6}$ (10)

$\cdot\mathrm{NH_2} + \cdot\mathrm{NH_2} \xrightarrow{M} \mathrm{N_2H_4}$ (11)

$\cdot\mathrm{CH_3} + \cdot\mathrm{NH_2} \xrightarrow{M} \mathrm{CH_3NH_2}$ (12)

Product	Conditions			Quantum yield	Quantum yield without NO*
	pressure (Torr)	irradiation time (s)	NO pressure (Torr)		
H_2	152	3500	16.0	3.2×10^{-4}	2×10^{-2}
	197	1500	10.3	9.9×10^{-4}	2×10^{-2}
CH_4	84.4	1500	2.8	9.6×10^{-5}	2×10^{-3}
	197	1500	10.3	1.2×10^{-5}	2×10^{-3}
$(CN)_2$	197	1500	10.3	1.6×10^{-1}	6×10^{-2}

Table 1. The effect of addition of NO on the quantum yields.
*The values in this column were estimated from Fig. 1 for the corresponding pressures of HCN.

In the course of long irradiation, a reddish brown substance became gradually noticeable, and after ten hours of irradiation it reduced the amount of absorbed light to 1/8 of the beginning. IR spectrum of the reddish brown substance, a soluble part in methanol, is shown in Fig. 2. Fig. 2 also gives an IR spectrum of a substance extracted with methanol from the products of methane-ammonia discharge5), for comparison. Both spectra are very similar and indicate the existence of =N-H, -C=N(conjugated), -N-H, $-NH_2$ and -C-H bonds, which were identified in IR spectra of polymerized products of hydrogen cyanide6)

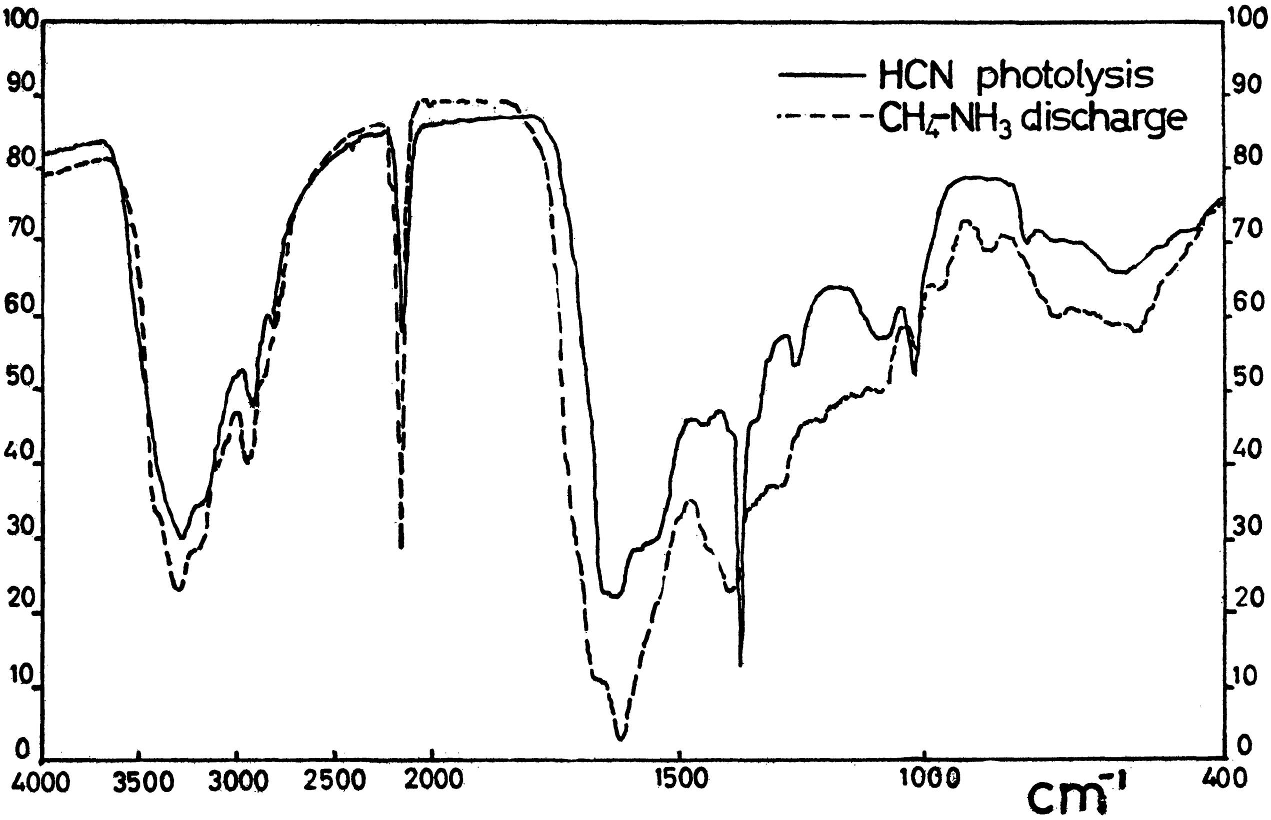

Fig. 2. IR spectra of the products of HCN photolysis and CH_4-NH_3 discharge.

References

1) For instance, C. Ponnamperuma, "The Origin of Prebiological Systems and of their Molecular Matrices", S. W. Fox ed., Academic Press, N.Y., p. 221 (1965), and R. A. Sanchez, J. P. Ferris and L. E. Orgel, J. Mol. Biol., 30, 223 (1967).

2) D. S. Villars, J. Am. Chem. Soc., 52, 61 (1930).

3 a) G. Herzberg and K. K. Innes, Can. J. Phys., 35, 842 (1957).

b) G. Herzberg, Molecular Spectra and Molecular Structure, Vol. 3, D. Van Nostrand Co., (1966).

4) A. Mele and H. Okabe, J. Chem. Phys., 51, 4798 (1969).

5) The sample was kindly provided by the curtesy of Prof. H. Noda,

6) M. J. D. Low and P. Ramamurthy, J. Res. Inst. Catalysis, Hokkaido Univ., 16, 535 (1968).

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