The Radiation Synthesis of Hydrogen Cyanide from the Nitrogen-ethylene System. The Effect of Fission-fragment Irradiation

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Upon irradiation by (FF+n+γ), the G(HCN) value from the nitrogen–ethylene system increased with the rise in the pressure, while upon γ and (n+γ) radiations it decreased. This pressure effect was explained in terms of the high concentration of the active species in the FF tracks. At a high pressure, Reaction (5) is considered to take place in the tracks;

$$N_2^+ + e^- \longrightarrow 2N \quad (5)$$

At low pressures, Reaction (6) predominates, as in the γ-ray radiolysis, over Reaction (5) even in the FF tracks,

$$N_2^+ + C_2H_4 \longrightarrow N_2 + C_2H_4^+ \quad (6)$$

and nitrogen molecule cations do not contribute to the formation of hydrogen cyanide.

Hydrogen cyanide is formed from the nitrogen-ethylene system by ionizing irradiation.[1–3] In a previous paper,[2] it was shown that both nitrogen atoms and excited nitrogen molecules were the precursors of hydrogen cyanide in the γ radiolysis.

In the present investigation, the hydrogen-cyanide formation was studied by means of ^{60}Co γ-rays and mixed reactor radiations (n+γ) and by fission-fragment (FF) radiation. The pressure dependence of the G(HCN) value by the FF irradiation differed significantly from that of the G(HCN) value by γ and (n+γ) irradiation. A new mechanism is proposed for the hydrogen-cyanide formation upon the FF irradiation, which is closely related to the structure of the FF tracks.

Experimental

Premixed gas (C_2H_4; 5.25% in N_2, pure gas mixed by Takachiho Chemical) and ethylene (Takachiho research grade, 99.9%) were used as reactant gases without further purification. A stainless steel capsule (inner vol., 43 ml) with a rupture plate at one end was used as the irradiation vessel. The capsule was washed successively with trichloroethylene, ethanol, and hot distilled water, and then vacuum dried. After evacuating the capsule to a vacuum of 5×10^{-3} Torr and purging three times with the reactant gas, a known amount of the gas was charged in the capsule, the pressure being measured by means of a stainless steel Bourdon gauge.

Irradiations were carried out by γ-rays from a 45 kCi ^{60}Co source or by means of reactor mixed radiations with or without an FF source in the Low Temperature Fissiochemical Loop (LTFL).[4] Without the FF source, neutrons and γ-rays, (n+γ), were absorbed by the reactant. With a piece of thin U-Pd alloy foil[5] set at the center of the capsule, the reactant was irradiated by fission fragments, neutrons, and γ-rays, (FF+n+γ). The absorbed dose was determined both by means of a gaseous chemical dosimeter[6] and by calculation using the data of the neutron flux and the average range of an FF in the gas.[7] The resultant dose rates were 0.9 Mrad/h (γ-rays), 5 Mrad/h (n+γ),[8] and 12—40 Mrad/h (FF+n+γ),[9] depending on the amount of the U-Pd alloy foil. The hydrogen cyanide formed was measured by the titration method using a 10^{-4} M mercuric nitrate solution, using copper diethyldithiocarbamate as an indicator.[2] The yields were measured at doses from 5 to 8 Mrad. The G(HCN) value was determined on the basis of the energy absorbed by nitrogen.

Results and Discussion

The Pressure Dependence of G(HCN). In the previous paper,[2] the G(HCN) value upon γ-ray irradiation was found to decrease with the rise in the total pressure from 0.05 to 1.5 atm. In this study, the pressure dependence of the G(HCN) value was examined on three radiations, γ, (n+γ), and (FF+n+γ). The results are shown in Fig. 1.

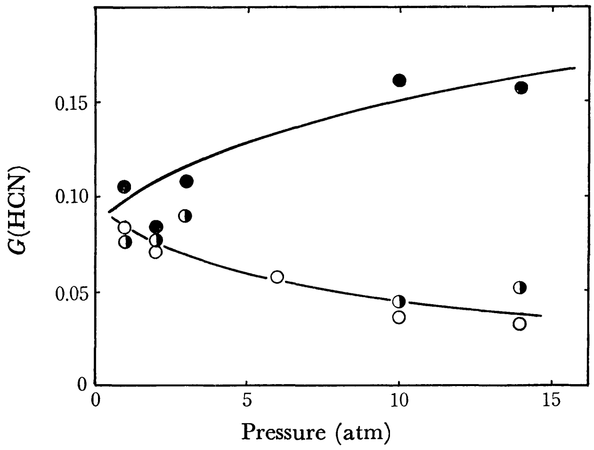

Fig. 1. Pressure effect on $G_{FFn\gamma}$, $G_{n\gamma}$, and G_γ.
N_2; 94.75%, C_2H_4; 5.25%, 43 ml stainless steel capsule, 5—8 Mrad. ●; $G_{FFn\gamma}$, 12—40 Mrad/h. ◑; $G_{n\gamma}$, 5 Mrad/h. ○; G_γ, 0.9 Mrad/h.

The G(HCN) values obtained by γ and by (n+γ) (G_γ and $G_{n\gamma}$, hereafter) decreased from 0.08 to 0.04 with the rise in the total pressure from 1 to 14 atm. This pressure dependence can be explained by the mechanism which was proposed previously[2] for the hydrogen cyanide formation in the γ-ray radiolysis:

$$N_2 \rightsquigarrow N, N_2^+, N_2^*, e^- \quad (1)$$

$$N_2^* \longrightarrow 2N \quad (2)$$

$$N_2^* + M \longrightarrow N_2 + M \quad (3)$$

$$N + C_2H_4 \longrightarrow HCN + CH_3 \quad (4)$$

The formation of nitrogen atoms by Reaction (2) is suppressed by the competitive Reaction (3) with a rise in the total pressure, resulting in a lowering of the

G(HCN) value.

The pressure dependence of the G(HCN) value upon (FF+n+γ) irradiation, $G_{FFn\gamma}$, differed distinctly from those of G_γ and $G_{n\gamma}$. The experimental $G_{FFn\gamma}$ value increased from 0.10 to 0.15 in the same pressure range. However, the ratio of the FF energy to the total energy was not exactly constant.[9] Therefore, for further discussion, the G(HCN) value obtained solely with FF, G_{FF}, was obtained by Eqs. (1) and (2), assuming that the experimental $G_{FFn\gamma}$ value is the mean value of the G_{FF} and $G_{n\gamma}$, weighted with the absorbed energies of the FF and (n+γ):

$$G_{FFn\gamma} = G_{FF}\varepsilon_{FF} + G_{n\gamma}\varepsilon_{n\gamma} \quad (1)$$

$$\varepsilon_{FF} + \varepsilon_{n\gamma} = 1 \quad (2)$$

where ε_{FF} or $\varepsilon_{n\gamma}$ is the ratio of the absorbed dose of FF or (n+γ) to the total dose. The $G_{n\gamma}$ value observed and the G_{FF} value thus calculated are shown in Table 1.

Table 1. Effect of pressure on G_{FF} and $G_{n\gamma}$[a)]

Pressure (atm)	1	3	10	14
$G_{n\gamma}$ (observed)	0.08	0.09	0.05	0.05
G_{FF} (calculated)[b)]	0.11	0.12	0.22	0.23

a) Absorbed dose; 5—8 Mrad, N_2; 94.75%, C_2H_4; 5.25%, 43 ml stainless steel capsule. b) Calculated by Eq. (1) in the text.

At 1 atm, the G_{FF} value, 0.11, is nearly equal to the $G_{n\gamma}$ value, 0.08, while at 14 atm the G_{FF} value is four times as large as the $G_{n\gamma}$ value. This pressure dependence of the G_{FF} value indicates that a quite different mechanism of the hydrogen-cyanide formation must be considered under the FF irradiation.

FF Tracks. According to Mozumder's model,[10] it is possible to detetmine the core radius and the temperature of the FF tracks in a condensed medium; the core radius is given by the impulse principle of Bohr or by the range of 100 eV electrons. In the gas phase, however, the latter is always longer than the former. By use of the model, the core radius of this system may be regarded as equal to a range of 100 eV electrons.

The concentration of the active species and the temperature in the tracks can be estimated if the core radius is determined. These values at 1 and 10 atm are shown in Table 2.

Table 2. FF tracks[a)]

Pressure p (atm)	Core radius r (Å)	Temperature elevation ΔT (°C)	Concentration of active species		
			$C_{N_2^+}=C_{e^-}$ (cm^{-3})	$C_{N_2^*}$ (cm^{-3})	C_N (cm^{-3})
1	1.2×10^4	0.2	2.6×10^{13}	4.4×10^{13}	4.4×10^{12}
10	1.2×10^3	15.1	2.6×10^{16}	4.4×10^{16}	4.4×10^{15}

a) Calculated in Appendix.

Chemical Reaction in the Core. The concentrations of active species in the core are several orders of magnitude higher than those of the γ-ray radiolysis (see Appendix). Because of this local high concentration of active species, the recombination of a nitrogen molecule cation[11—13] with an electron may be assumed in the FF track core:

$$N_2^+ + e^- \longrightarrow 2N \quad (5)$$

By Reaction (5), two kinds of nitrogen atoms, N(^{4}S) and N(^{2}D), are formed mainly,[14] and each state of the nitrogen atom is known to react with ethylene to form hydrogen cyanide[15,16], according to Reaction (4).

In the γ-ray radiolysis, the charge on a nitrogen cation is transferred to an ethylene molecule, and no contribution is expected to the hydrogen cyanide formation:

$$N_2^+ + C_2H_4 \longrightarrow N_2 + C_2H_4^+ \quad (6)$$

In the FF radiolysis, Reactions (5) and (6) can compete with each other. The rates of the two reactions in the track core were calculated at 1 and 10 atm, as is shown in Table 3. At 1 atm, Reaction (5) is much slower than Reaction (6) even in the track core, and Reaction (5) can be neglected, as in the γ-ray radiolysis. At 10 atm, however, Reaction (5) predominates over Reaction (6), resulting in the formation of excess nitrogen atoms. The higher the total pressure, the more excess nitrogen atoms are formed in the core by this mechanism. This is in qualitative agreement with the experimental results (Table 1).

Table 3. Reaction rate in the track core

Pressure (atm)	rate of reaction (5);[a)] $N_2^+ + e^- \rightarrow 2N$ (cm^{-3}·s^{-1})	rate of reaction (6);[b)] $N_2^+ + C_2H_4 \rightarrow N_2 + C_2H_4^+$ (cm^{-3}·s^{-1})
1	2.0×10^{20}	1.0×10^{22}
10	2.0×10^{26}	1.0×10^{26}

The concentrations of N_2^+ and e^- are given in Table 2. The ethylene concentration is 1.2×10^{18} and 1.2×10^{19} cm^{-3} at 1 and 10 atm (5% C_2H_4 in N_2).
a) Rate constant of reaction (5); $k_5=3\times10^{-7}$ cm^3·s^{-1}.[16] b) Rate constant of reaction (6); $k_6=3\times10^{-10}$ cm^3·s^{-1}, is estimated from similar reactions.[19]

The Role of Ethylene Molecules. The effect of the ethylene concentration on the $G_{FFn\gamma}$ value was studied in order to clarify the role of ethylene molecules in the formation of hydrogen cyanide upon the FF irradiation. If the mechanism of hydrogen-cyanide formation

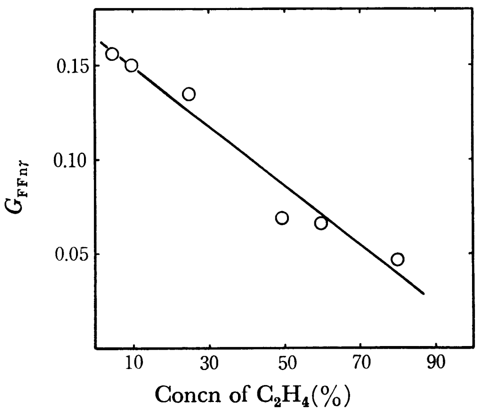

Fig. 2. Effect of ethylene concentration on $G_{FFn\gamma}$.[a)] (FF+n+γ); 12 Mrad/h, 6.8 Mrad, ε_{FF}; 0.66, N_2+C_2H_4; 14 atm in 43 ml stainless steel capsule.
a) The G(HCN) value was calculated on the basis of the energy absorbed by nitrogen.

proposed above holds, the G(HCN) value should decrease with the rise in the ethylene concentration because of Reaction (6).

As is shown in Fig. 2, the G(HCN) value actually decreased with the ethylene concentration. Thus, this mechanism is again in agreement with the experimental results.

Local Temperature Effect. Since a small increase in the G_γ value has been observed upon reaction-temperature elevation at a low total pressure,[2] the effect of the local temperature rise within the FF track core might be expected on the G_{FF} value also at the high total pressure studied. The measured G_γ value was indeed found to increase as the temperature was raised, as is shown in Fig. 3. However, the increase was not large enough to explain the high G_{FF} value obtained. The G_γ values were 0.04 and 0.07 at 40 and 400 °C respectively.

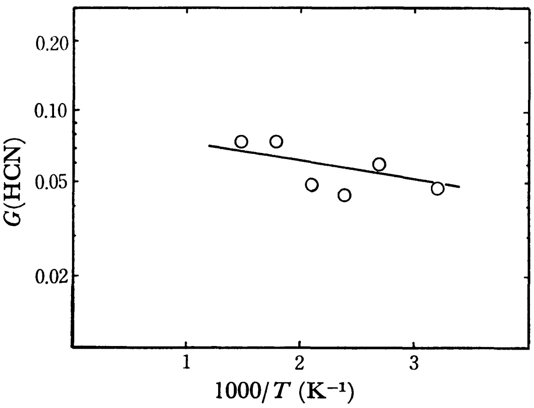

Fig. 3. Arrhenius' plot of G_γ.
γ-rays; 0.9 Mrad/h, 4.3 Mrad. N_2; 15.1 g/l, C_2H_4; 5.25% in N_2.

The temperature effect in this system can be neglected because of the small increase in the G_γ value with the reaction temperature elevation and because of the low temperature rise in the track cores (Table 2).

Appendix

Radius and Temperature of the Track Cores.[10] The radius of the FF track cores in this system is given by this equation: $r=r_0\rho_0/\rho$, where r_0 is the range of 100 eV electrons in water (15 Å), ρ_0 and ρ, the desities of water and the reactant gas. The temperature rise in the cores is given by this equation: $\Delta T=S/\pi C_v r^2$, where S is the energy loss per unit length (0.4 eV/Å$=0.64\times10^{-11}$ J/cm at 1 atm,[17] and 4 eV/Å$=6.4\times10^{-11}$ J/cm at 10 atm), and C_v, the specific heat at a constant volume (0.75 J/deg·g). Thus, $\Delta T=0.2$ and 15.1 °C at 1 and 10 atm.

Concentrations of Active Species in the Cores. The concentration of an active species, C_A, is given by this equation: $C_A=Sg_A/100\,\pi r^2$, where g_A is the initial G(A) value. Using appropriate g_A value ($g_{N_2^+}=g_{e^-}=3$, $g_{N_2^*}=5$, and $g_N=0.5$[8]), the concentrations of these active species are found to be as is shown in Table 2. The ratio is $(N)/(N_2)=1.8\times10^{-7}$ at 1 atm. This value is several orders of magnitude greater than the corresponding one in the γ-ray radiolysis (0.9×10^{-13}).[2]

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8) The (n+γ) rays (total, 5.0 Mrad/h) were constituted of γ-rays (4.1 Mrad/h), fast neutrons (*ca.* 0.01 Mrad/h), and protons arising from the nuclear reaction of thermal neutons, ^{14}N(n,p)^{14}C (0.9 Mrad/h).

9) In the case of (FF+n+γ) irradiation, the area of the foil was determined so that the ratio of the absorbed dose by FF to the total dose, ε_{FF}, fell in a relatively narrow range, 0.60—0.87.

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11) Because of the fast clustering reaction: $N_2^+ + 2N_2 \rightarrow N_4^+ + N_2$ ($k=6\times10^{-29}$ cm^{-6} s^{-1}), the recombination of both N_2^+ and N_4^+ with electrons may be considered. Also, the formation of N atoms by the recombination of N_4^+ with an electron is energetically possible because of the low binding energy of N_2^+ with N_2 (0.5 eV).[12] However, the equilibrium concentration of N_4^+ is presumably lower than that of N_2^+, as was estimated in the case of O_2^+—O_4^+.[13]

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