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Radiation Synthesis of Hydrogen Cyanide from Nitrogen-Ethylene System. Effect of Temperature, Gas Density, and Reactor Wall

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The rate of formation of hydrogen cyanide from the nitrogen–ethylene system by ^{60}Co gamma rays was found to depend on irradiation temperature, gas density, gas composition, and the nature of the wall surface of the reaction vessel. Above 100 °C, the G(HCN) value increased with the rise of temperature. Below 100 °C, the G(HCN) value remained constant down to -196 °C. In the temperature range from 400 °C to -196 °C, it increased with reduction of nitrogen gas density. The largest G(HCN) value obtained was 2.0. In certain cases, the wall surface influenced the suppression of hydrogen cyanide formation. As an active species responsible for hydrogen cyanide formation, excited nitrogen molecules are proposed in addition to nitrogen atoms. Excited nitrogen molecules are decomposed to nitrogen atoms with small activation energy or deactivated by collision with other molecules. They play an important role in cyanide formation at low pressures and at high irradiation temperatures.

Radiation reactions of activated nitrogen have been investigated in many systems. In the radiolytic isotopic exchange reaction of nitrogen, the G-value of the exchange reaction is in the range 9—19.[1–3] The large exchange G-value seems to indicate that nitrogen molecules are activated by radiation. Ammonia synthesis from the nitrogen–hydrogen system,[4] nitrogen fixation from the nitrogen–oxygen system[5] and ammonium synthesis from the air–water system[6] are also reported. The G-values of nitrogen fixation reactions in these systems are generally about one, and reach three at most.

As a radiation reaction involving activated nitrogen, formation of hydrogen cyanide from nitrogen–ethylene system has been studies by Oka *et al.*, and the G-values of about 0.5 and 0.2 were reported for the reactions in gas phase and in liquid nitrogen.[7–9] In order to elucidate the reactivity of the radiation activated nitrogen and attain higher yields of cyanide, we investigated in detail the effects of irradiation temperature, density, gas composition, and the nature of the wall surfaces of reaction vessels.

Experimental

Nitrogen gas (purity; 99.9995%, oxygen content; 0.5 ppm, Nihon Sanso Co.) was used after removal of condensable gases with a liquid nitrogen trap. Ethylene gas (purity; 99.9%, acetylene content; 1 ppm, oxygen content; 0 ppm, Nihon Sekiyukagaku Co.) was purified by trap to trap distillation in a vacuum line. The two gases mixed in a vacuum line were analysed with a mass spectrometer and the absence of oxygen, water or carbon dioxide was confirmed.

Four kinds of irradiation ampoules, *i. e.* 170 ml Pyrex glass, 64 ml Pyrex glass, 64 ml quartz glass, and 55 ml stainless

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[1] M. Anbar and P. Perlstein, *J. Chem. Phys.*, **68**, 1234 (1964).

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[3] R. Shimozawa and K. Oshima, Proceedings for the 10th Discussion Meeting of Radiation Chemistry, Hiroshima (October, 1967).

[4] C. H. Cheek and V. J. Linnenbon, *J. Phys. Chem.*, **62**, 1475 (1958).

[5] M. Steinberg, *Chem. Eng. Progr.*, **62**, (9) 105 (1966).

[6] S. Sato and M. Steinberg, BNL-13692 (1969).

[7] T. Oka, R. Kato, S. Sato, and S. Shida, This Bulletin, **41**, 2192 (1968).

[8] T. Oka and S. Sato, *ibid.*, **42**, 582 (1969).

[9] T. Oka, Y. Suda, and S. Sato, *ibid.*, **42**, 3083 (1969).

steel, were used. The glass ampoules were washed in two ways, by washing them thoroughly with only distilled water or by immersing them in concentrated nitric acid solution for several days and washing with distilled water four or five times. The stainless steel ampoules were immersed in a rust removing reagent (Dipsol ST-305 solution) for 5—10 minutes, washed with water, treated with 20% NaCN solution and washed with water again. The ampoules were evacuated to a vacuum of 1×10^{-4} Torr while they were being heated. Known amounts of gases were then charged into the ampoules, pressure being measured with a quartz Bourdon gage.

Irradiation of the gases was carried out with ^{60}Co-γ rays. The dose rate of γ-rays was measured with a Fricke dosimeter. The absorbed dose in nitrogen gas was estimated from the Fricke dosimetry corrected for the ratio of stopping power of nitrogen to that of glass against secondary electrons.[10–11] The absorbed dose in ethylene was neglected in the calculation of *G*(HCN). High temperature irradiation was carried out in an electric furnace, in which the temperature was controlled to an accuracy of ±2 °C. Low temperature irradiations were carried out in liquid nitrogen (−196 °C) and in dry ice (−78 °C).

Hydrogen cyanide was measured as follows. The product was trapped at the bottom of the irradiated ampoule with a liquid nitrogen trap. The top of the ampoule was then broken and 10 ml of 1/100 N NaOH solution quickly poured into the ampoule to dissolve hydrogen cyanide. In the case of high ethylene partial pressure, a device was connected to the top of the ampoule in order not to release hydrogen cyanide. After purging the dissolved ethylene and other hydrocarbons by bubbling with nitrogen gas about 5 minutes, hydrogen cyanide remaining in the 1/100 N NaOH solution was titrated with 10^{-4} M mercuric nitrate solution, using 1 ml of 38 ppm carbon tetrachloride solution of copper diethyldithiocarbamate[12] as an indicator. Hydrogen cyanide in the solution was also analysed with an electrode potentiometer (Cyanometer CN-IA, Toa Electronics Ltd.) for confirmation of the titration method. The two methods gave the same result.

Results

When nitrogen–ethylene mixtures are irradiated, acetylene, *n*-butane, ethane, and propane are formed besides hydrogen cyanide. Hydrogen cyanide formation was studied in connection with reaction of nitrogen activated by radiation. It was found to depend on the irradiation temperature, the density, and composition of the mixed gas and the nature of the wall.

The formation of hydrogen cyanide at various temperatures, shown in Fig. 1, is linear to the absorbed radiation energy in nitrogen gas. Estimated errors in titration are also given. The *G*(HCN) values calculated from the slopes were 1.9 at 400 °C, 1.5 at 300 °C, 0.8_0 at 100 °C and 0.7_3 at −196 °C. The *G*(HCN) value 0.7_3 at −196° C was very close to the one, 0.8_0 at 100 °C. This is of interest when we consider the small partial pressure of ethylene at −196 °C.[13]

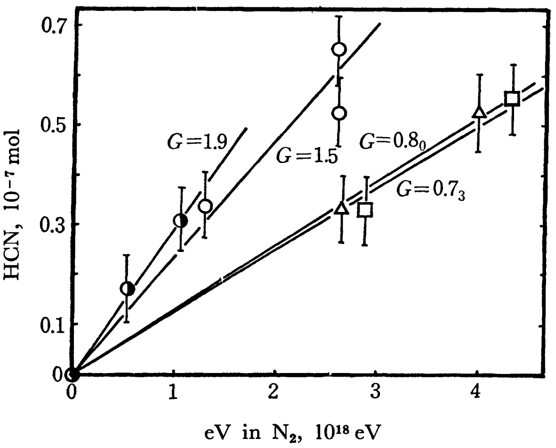

Fig. 1. HCN formation from N_2-C_2H_4 at various temperatures.
N_2; 0.11 g/l, C_2H_4=0.075, γ-rays; 6.8×10^5 R/hr, 0—6 hr irradiated.
◐; 400 °C, ○; 300 °C, △; 100 °C, □; −196 °C

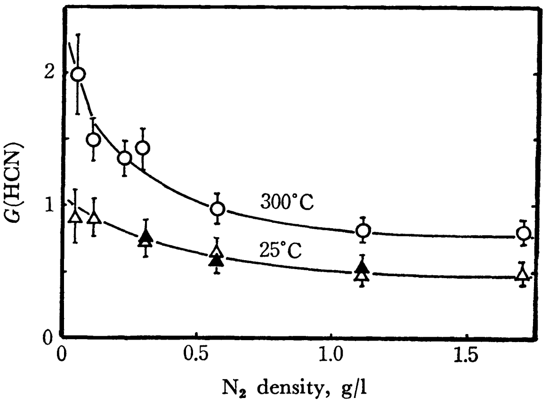

Fig. 2. N_2 gas density dependence of *G*(HCN).
γ-rays; 6.8×10^5 R/hr, 0—6 hr irradiated, C_2H_4/N_2=0.075.
○; irradiated at 300 °C in 170 ml Pyrex ampoule.
△; irradiated at 25 °C in 170 ml Pyrex ampoule.
▲; irradiated at 25 °C in 64 ml Pyrex ampoule.

The *G*(HCN) values at 300 °C and 25 °C are shown in Fig. 2 as a function of nitrogen gas density, for a constant C_2H_4/N_2 ratio of 0.075. At both temperatures the *G*-values depended on the density of gas and became larger as the density was reduced. At 25 °C and at high nitrogen gas density, the *G*-values converged to 0.5, in agreement with a reported value.[7] The density dependence might be attributed to heterogeneous reactions on the wall surface of the reaction vessels. Two kinds of Pyrex ampoules with different surface to volume ratios were used to examine the effect of heterogeneous reaction. However, no difference in density dependence of *G*(HCN) was seen between the two ampoules within the experimental error (Fig. 2).

At 300 °C, the *G*(HCN) value converged to 0.8 at high nitrogen gas density, becoming as large as 2.0

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[10] T. E. Burlin, "Radiation Dosimetry" Vol. 1, ed. by F. H. Attix, W. C. Roesch, and E. Tochilin, Academic press, New York (1968), p. 331.

[11] G. R. A. Johnson, *J. Inorg. Nucl. Chem.*, **24**, 461 (1962); D. W. Huyton and T. W. Woodward, *Radiation Res. Rev.*, **2**, 205, (1970).

[12] Y. Tanaka and S. Yamamoto, *Bunseki Kagaku*, **9**, 6 (1960).

[13] At −196 °C the vapor pressure of ethylene becomes 6.5×10^{-4} Torr. Ethylene in the irradiation ampoules is condensed on the wall surface for the most part, and the C_2H_4/N_2 ratio in gas phase is equal to 3.3×10^{-5}, which is much smaller than the one, 7.5×10^{-2} at other temperatures.

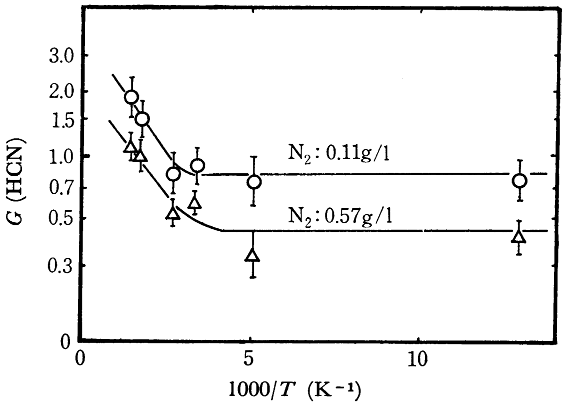

Fig. 3. Arrhenius' plot of G(HCN).
γ-rays; 6.8×10^6 R/hr, 0—6 hr irradiated, $C_2H_4/N_2=0.075$.
○; N_2 gas density $=0.11$ g/l.
△; N_2 gas density $=0.57$ g/l.

(±0.3) as the density was reduced to 0.054 g/l. The latter value is one of the greatest obtained experimentally. At both temperatures, a constant value was reached with high gas density, and became larger as the density was reduced. However, the extent of increase in G(HCN) at 300 °C was greater than that at 25 °C.

Arrhenius' plots of G(HCN) are shown in Fig. 3 for two nitrogen gas densities, 0.11 and 0.57 g/l, with a constant C_2H_4/N_2 ratio, 0.075. All the plotted G(HCN) values were obtained from the slopes of the cyanide formation as in Fig. 1. At low gas density, the G(HCN) values were larger than those at high density in the whole temperature range, −196—400 °C, but the temperature dependences corresponding to the two gas densities were similar. Above 100 °C, the G(HCN) values increased with an apparent activation energy of 1.2 kcal/mol, and below 100 °C, they were constant down to −196 °C. This indicates that the mechanism of hydrogen cyanide formation at high temperature differs from that at low temperature.

The G(HCN) value is known to be independent of ethylene partial pressure in the C_2H_4/N_2 ratio range 0.1—0.001.[7,14] The variation of G(HCN) with higher ethylene partial pressures is shown in Table 1. Since the ionization potential of nitrogen, 15.6 eV, is fairly larger than that of ethylene, 10.6 eV, it is not probable that nitrogen molecules are activated by the excited ethylene molecules to form hydrogen cyanide.[15] In the calculation of the G(HCN) value, only the energy absorbed by nitrogen was counted and that by ethylene neglected.

The G(HCN) values at 25 °C (Table 1) decreased from 0.6_4 to 0.3_0 as the C_2H_4/N_2 ratio was increased from 0.036 to 1.92. Decreasing G(HCN) values were obtained with both high nitrogen gas density and high ethylene partial pressure, the tendency being the same at 25 °C and at 300 °C.

TABLE 1. G(HCN)[a] DEPENDENCE ON C_2H_4/N_2 RATIO AT 300 AND 25 °C

C_2H_4/N_2	G(HCN), 300 °C	G(HCN), 25 °C
0.036	—	0.6_4
0.075	0.9_4	0.6_1
0.36	—	0.5_2
0.72	—	0.4_6
1.09	—	0.3_9
1.92	0.6_7	0.3_0

γ-rays; 6.8×10^5 R/hr, 0—2 hr irradiated, N_2; 0.57 g/l in 170 ml ampoules.
a) Calculation of G(HCN) is based on the energy absorbed by the nitrogen.

TABLE 2. WALL EFFECT

Reactor	G(HCN)
Pyrex A[a]	0.5±0.05
Pyrex B[b]	0.5±0.05
Quartz A[c]	0.5±0.1
Quartz B[d]	0.3±0.1
Steel[e]	0.3±0.1

$C_2H_4/N_4=0.07\pm0.02$, N_2; 1.1 g/l, γ-rays; 0—3×10^6 Rad, 25 °C.
a) 170 ml Pyrex ampoule washed with distilled water.
b) 64 ml Pyrex ampoule washed with distilled water.
c) 64 ml quartz ampoule washed with distilled water.
d) 64 ml quartz ampoule washed with concentrated nitric acid solution and distilled water.
e) 55 ml stainless steel ampoule, treated with rust removing reagent (Dipsol ST-305 solution) and with NaCN 20% solution, and then washed with water.

Ampoules of different size and material were used as the irradiation vessel to investigate the surface effect on hydrogen cyanide formation under the same experimental conditions. The results are shown in Table 2. In the Pyrex and quartz ampolues washed only with distilled water, the G(HCN) values were 0.5±0.1. In the quartz and stainless steel ampoules treated with nitric acid and washed with water, they were 0.3±0.1, reproducibility being poor.

Discussion

The results show that the formation of hydrogen cyanide depends on the irradiation temperature, the density, composition of the mixed gas and the wall. The mechanism of the formation of hydrogen cyanide will be discussed.

Nitrogen molecules are activated by radiation to form a variety of active species.[19-20]

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14) Y. Ikezoe, O. Tokunaga, N. Moriyama, R. Shimozawa, T. Tamura, and A. Danno, JAERI-memo 3506 (1969).

15) Excitation spectrum of ethylene[16-17] shows that ethylene can be excited to higher energy levels than dissociation energy 9.76 eV, and ionization potential of nitrogen 15.6 eV. Such highly excited ethylene can dissociate or ionize a nitrogen molecule. However, the direct ionization, autoionization, and dissociation process of ethylene are much faster[18] than the nitrogen activation process by the excited ethylene in our experimental conditions. Thus, the ethylene molecules directly activated by radiation seem to make no contribution to cyanide formation.

16) Y. Hatano, This Bulletin, **41**, 1126 (1968).

17) E. N. Lassettre and S. A. Francis, *J. Chem. Phys.*, **40**, 1208 (1964).

18) S. Shida, *Radioisotopes*, **19**, 92 (1970).

19) S. Ya. Pshezhetskii and M. T. Dmitriev, *At. Energ. (U. S. S. R.)*, **3**, 350 (1957).

20) S. Dondes, P. Harteck, and C. Kunz, *Z. Naturforschg.* **19**, 6 (1964).

$$N_2 \rightsquigarrow N_2^+,\ N^+,\ N,\ N_2^*,\ N_2^{+*},\ e^- \tag{1}$$

Nitrogen molecule ions N_2^+ are thought to take no part in the formation of hydrogen cyanide, on account of their fast charge transfer reaction with ethylene.[7]

$$N_2^+ + C_2H_4 \longrightarrow N_2 + C_2H_4^+ \tag{2}$$

Thus an active species considered able to take part in the formation of hydrogen cyanide should be sought from nitrogen atoms, atom ions, excited nitrogen molecules, and excited molecule ions.

In the study of active nitrogen produced by electric discharge, hydrogen cyanide has been said to be formed by the following reactions.[21–23]

$$N + C_2H_4 \longrightarrow HCN + CH_3 \tag{3}$$

$$N + CH_3 \longrightarrow HCN + 2H \tag{4}$$

Reaction (4) is faster in electric discharge but can be neglected in the case of radiolysis, because of low concentration of active species.[24] As the reaction of hydrogen cyanide formation by radiation, the following reaction has been proposed by Oka *et al.*[7]

$$N(\text{or } N^+) + C_2H_4 \rightarrow HCN + CH_3\cdot(\text{or } CH_3^+) \tag{3'}$$

They found the G(HCN) value to be independent of nitrogen pressure in the range 250—750 Torr and explained the phenomena by this reaction.

Our results, however, show that the G(HCN) value depends both on gas density and irradiation temperature. It therefore seems apparent that a mechanism other than reaction (3′) is important for our experimental conditions.

Absorbed Dose of Gas in an Ampoule at Low Gas Density. Before discussing the mechanism of hydrogen cyanide formation, absorbed dose at low gas density should be considered. Absorbed dose of high density gas in an ampoule is proportional to the electron density, and that of low density to the stopping power ratio to the secondary electrons.[10] In general, absorbed dose varies as the gas density varies. In the case of nitrogen gas in a glass ampoule, both the stopping power ratios of nitrogen and of glass are nearly equal, and the absorbed dose of nitrogen can be obtained from the electron density of nitrogen irrespective of nitrogen gas density.[11] The difference in the G(HCN) value at high and low nitrogen gas density in Fig. 3 can not be explained by the deviation of absorbed doses at low gas density.

Excited Nitrogen Molecule. Heterogeneous reactions on the wall of the Pyrex glass ampoules were not detected (Fig. 2). We might thus assume the following reactions to explain the gas density dependence of G(HCN) value.

$$N_2^* \ (\text{or } N_2^{+*}) \longrightarrow N + N \ (\text{or } N^+) \tag{5}$$

$$N_2^* \ (\text{or } N_2^{+*}) + M \longrightarrow N_2 + M \ (\text{or } M^+) \tag{6}$$

Reaction (5) is predominant at low gas density, and reaction (6) at high gas density.

Nitrogen atom formed by reaction (5) then reacts with ethylene to form hydrogen cyanide. This means excited nitrogen molecules and/or excited nitrogen molecule ions in addition to the atoms and/or the atom ions can be precursors of hydrogen cyanide. The difference in G(HCN) values at low and high nitrogen gas density, $\Delta G_{25^\circ\mathrm{C}}=0.4$ and $\Delta G_{300^\circ\mathrm{C}}=1.2$, can be explained if they correspond to the initial G-value of excitation of nitrogen molecules, $g(N_2^*$ or $N_2^{+*})$.[26]

It is of interest to see whether the excited nitrogen molecules form cyanide by reactions (5) and (3′) or directly by the following reaction.

$$N_2^* \ (\text{or } N_2^{+*}) + C_2H_4 \longrightarrow HCN + \text{others} \tag{7}$$

The result given in Table 1 indicates that reaction (7) does not take place at 25 °C and 300 °C, and the excited nitrogen molecules are deactivated by ethylene by the following reaction.

$$N_2^* \ (\text{or } N_2^{+*}) + C_2H_4 \rightarrow N_2 + C_2H_4^* \ (\text{or } C_2H_4^{+*}) \tag{6'}$$

Excited nitrogen molecules can not directly form hydrogen cyanide but after reaction (5), they react to form hydrogen cyanide.

Irradiation Temperature Dependence. At temperatures above 100 °C, the G-values were dependent on temperature, but at lower temperatures they were independent of temperature (Fig. 3). This indicates that an elementary reaction which requires some activation energy is the rate-determining step in the cyanide formation reaction at high temperatures. The nitrogen gas density dependence of G(HCN)

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[21] G. Paraskevopoulos and C. A. Winkler, *J. Phys. Chem.*, **71**, 947 (1967).

[22] J. T. Herron, *J. Phys. Chem.*, **69**, 2736, (1965).

[23] B. Brocklehurst and K. R. Jennings, "Progress in Reaction Kinetics," Vol. 4 ed. by G. Porter, Pergamon Press, Oxford, p. 1.

[24] Nitrogen atom concentration in our experimental conditions is estimated. When partial pressure of nitrogen is 1 atm, ethylene 0.1 atom, dose rate of γ-rays 10^6 Rad/hr, the initial G (N) value 0.5 and the rate constant of disappearance reaction of nitrogen atoms, reaction (3), ($k=1\times10^7$ litre $\mathrm{mol^{-1}\ s^{-1}}$)[23], the rate of nitrogen atom formation per one mole nitrogen κ, is

$$\kappa=(10^6\ \mathrm{Rad/hr})\times(1/3600\ \mathrm{h/s})\times(6.24\times10^{13}\ \mathrm{eV/g\ Rad})$$
$$\times(28\ \mathrm{g/N_2\ mole})\times(G(\mathrm{N})/100\ \mathrm{atom/eV})=4.85\times10^{15}\,G(\mathrm{N})$$
$$\mathrm{atom/N_2\ mol\ sec}=2.43\times10^{15}\ \mathrm{atom/N_2\ mol\ sec}$$

The mean life time of nitrogen atom τ, is

$$\tau=1/k[C_2H_4]=2.2\times10^{-5}\ \mathrm{s}.$$

The mean concentration of nitrogen atom (N), is

$$(\mathrm{N})=\kappa\tau=5.4\times10^{10}\ \mathrm{atom/N_2\ mol}.$$

The ratio, $(\mathrm{N})/(\mathrm{N_2})=5.4\times10^{10}/6\times10^{23}=0.9\times10^{-13}$. This value is much smaller than 1×10^{-1} in the electric discharge experiment.[25]

[25] D. R. Safrany and W. Jaster, *J. Phys. Chem.*, **72**, 518 (1968).

[26] It is possible to calculate a $g(N_2^*)$ value with an excitation energy range 11.4—13.6 eV, which lies between the dissociation energy and the ionization potential of nitrogen molecules. As the oscillator strength in the range is known to be 0.87,[27] the $g(N_2^*$, 11.4—13.6) value can be calculated by the equation.[28]

$$g(N_2^*,\ 11.4\text{—}13.6)=\frac{(M_{11.4-13.6})^2}{(M_i')^2}\times\frac{100}{W}$$

where $(M_{11.4-13.6})^2$ is the dipole matrix element squared for the excitation energy range and is equal to $fR/E(=0.95)$, R Rydberg constant, E excitation energy (taken as an average in the energy range), $(M_i')^2$ the dipole matrix element squared for ionization (=3.85), and W the average energy for an ion pair production (=34.4 eV). Thus $g(N_2^*;$ 11.4—13.6) is calculated to be 0.72.

[27] S. M. Silverman and E. N. Lassettre, *J. Chem. Phys.*, **42**, 3420 (1965).

[28] C. E. Klots, "Fundamental Processes in Radiation Chemistry," ed. by P. Ausloos, Interscience Publishers, New York, N. Y. (1968), p. 1.

was more remarkable at high temperatures than at low. Thus, excited nitrogen molecules seem to play a more important role at high temperatures making reaction (5) require some activation energy.

G(HCN) values reached constant values at a high gas density, but differed with differing temperature (Fig. 2). The G(HCN) value became constant at low temperature, but also took a different value at a different gas density (Fig. 3). This seems to indicate that two kinds of nitrogen atoms, one directly formed by radiation according to reaction (1) and the other indirectly formed by radiation according to reactions (1) and (5), can not be distinguished clearly from each other.

Wall Effect. In glass ampoules washed with only distilled water, the G(HCN) value was constant irrespective of ampoule volume, but in glass ampoules and stainless steel ampoules treated with nitric acid solution, cyanide formation was suppressed. In the former case, the surface/volume ratio did not differ so much that it is difficult to say whether the wall surface affects cyanide formation at all. In the latter case, the suppression may be due either to the active species being trapped on the wall surface or to hydrogen cyanide formed being decomposed on the surface.