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The Formation of Nitrogeneous Compounds in the γ-Radiolyses of Liquid Nitrogen Solutions of Hydrogen, Methane, and Ethane

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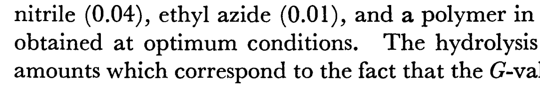
The γ-radiolyses of liquid nitrogen solutions of hydrogen, methane, and ethane have been reinvestigated. A complete survey of nitrogen-containing products has been attempted. The nitrogeneous compounds observed were ammonia (0.7) and hydrogen azide (0.02) in the case of hydrogen, ammonia (0.3), hydrogen cyanide (0.1), methyl azide (0.01), and a polymer in the case of methane, and ammonia (0.3), hydrogen cyanide (0.05), acetonitrile (0.04), ethyl azide (0.01), and a polymer in the case of ethane. The values in parentheses are the *G*-values obtained at optimum conditions. The hydrolysis of the polymer obtained with methane gave formaldehyde in amounts which correspond to the fact that the *G*-value of the nitrogen atoms which were converted into the polymer is about 1.0. In order to explain these results, possible reaction mechanisms are discussed.

The reactions of nitrogen atoms with hydrocarbons have been investigated in the gas phase, using active nitrogen produced in a discharge;[1] however, probably because of the low pressure and of the high temperature, more than 90% of the nitrogeneous compounds observed were hydrogen cyanide, irrespective of the hydrocarbon used. Consequently, it was almost impossible to elucidate any details of the reaction mechanism.

A few years ago, our laboratory started to use the γ-radiolysis of liquid nitrogen as the source of nitrogen atoms and studied the reactions with several olefins which are soluble in liquid nitrogen with the hope that the addition products might not decompose into hydrogen cyanide.[2] In fact, we observed the formations of acetonitrile, propionitrile, and acrylonitrile, respectively, in the reactions with propylene, 1-butene, and allene, and we could propose a generalized reaction mechanism:[3]



$$\mathrm{RCH{=}CH_2 + N \rightarrow R\text{-}\overset{H}{\underset{N}{C}}\text{-}CH_2 \rightarrow RCN + CH_3.}$$

However, the *G*-values of these nitrile compounds, including hydrogen cyanide obtained in the reaction with ethylene were very small—less than 0.2. During these measurements, we recognized the formation of a polymer and measured the *G*-value of the nitrogen atoms which were converted into the polymer by using Conway's method. This method is one of the techniques frequently used in biochemistry. A sample containing amine and/or imine is hydrolyzed in an alkaline solution and the ammonia evolved is absorbed in dilute sulfuric acid in a specially designed vessel, and then the amount of ammonia is measured photometrically. The *G*-value of nitrogen atoms thus estimated was strongly dependent upon the hydrocarbons used and ranged from 0.1 to 0.7.[4] We tentatively explained this dependency to be due to the solubilities of hydrocarbons into liquid nitrogen.

In a short note, Siderer and Sato reported the results obtained in the γ-radiolysis of the liquid nitrogen solution of methane. The *G*-value of hydrogen cyanide was 0.08 at the optimum condition, while that of ammonia obtained by using Conway's method was 0.6.[5] On the basis of these results, they suggested that the nitrogen atoms which give nitrile compounds are not in the ground state, ^4S, but in the excited state, ^2D and/or ^2P, while the nitrogen atoms in the ground state lead to the formation of a basic polymer.

Experimental

The dried high-purity nitrogen was purchased from the Takachiho Shoji Co., and was used after having been passed through sulfuric acid (Yotsuhata Chemical Co.). The hydrogen, methane, ethane, ammonia, and various hydrocarbons used for identification were also purchased from the Takachiho Shoji Co. The hydrogen cyanide was synthesized from sodium cyanide and sulfuric acid. The nitrile compounds were supplied by the Tokyo Kasei Co. The sodium 4,5-dihydroxy-2,7-naphthalenedisulfonate used for the quantitative estimation of formaldehyde was purchased from the Wako Chemical Co.

The samples for γ-irradiation were prepared in the same manner as has been described before;[5] *i.e.*, a known amount of hydrogen, methane, or ethane was first introduced into a sampling tube 20 cm long and 3 cm in diameter. The pressure was measured by means of an oil manometer. Then pure nitrogen was introduced into the tube at 77 K under the pressure a little higher than the atmosphere. The nitrogen was then easily liquefied. The amount of the liquid was measured by the scale on the sampling tube. Since the amounts of substrates, hydrogen, methane, and ethane introduced were small, all of the gases were assumed to be dissolved into the liquid nitrogen.[6]

The samples thus prepared were irradiated by ^{60}Co γ-rays in a liquid nitrogen-Dewar flask at a dose rate of about 1.2×10^6 R h^{-1}, usually for 1 h. After irradiation, the sampling tube was connected to a vacuum system and the inside was slowly pumped out at 77 K. Usually two hours were taken for complete evacuation. The products thus obtained were subjected to analysis.

In order to identify the volatile products, use was made of a quadrupole mass-spectrometer (Nichiden-Varian TE-600) after separating the products with a gas chromatograph, the column of which was made of 6 m Silicone SE-52 supported by Uniport KS 60—80 mesh 80% w/w. Helium was used for the carrier gas.

Several analytical methods were applied to the identification of the polymer obtained in the reaction with methane: mass-spectrometry for the solid state, NMR spectroscopy, and thin layer chromatography. However, no conclusive results could be obtained except that the polymer contains N–H bonds, which was shown by the NMR spectroscopy.

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Since the polymer was easily hydrolyzed with a dilute aqueous solution of hydrochloric acid to produce formaldehyde, we measured the amount of the aldehyde photometrically using sodium 4,5-dihydroxy-2,7-naphthalenedisulfonate as a chromophoric reagent.[7]

Results

Hydrogen. As the reaction products, we observed two compounds: ammonia and hydrogen azide. Both compounds were identified by the mass-spectra. Figure 1 shows the *G*-values of the two products as functions of the concentration of hydrogen introduced into the sampling tube. The extrapolation of the plots between $1/G(NH_3)$ and $1/[H_2]$ gave $G(NH_3) = 0.7$ at the infinite concentration of hydrogen. We looked for hydrazine as a product, since it is another simple compound composed of nitrogen and hydrogen atoms; however, we could not observe the formation of this compound.

Methane. Ammonia, ethane, hydrogen cyanide, methyl azide, and small amounts of acetonitrile and propane were observed as volatile products. As is shown in Fig. 2, the *G*-values of ammonia and ethane showed a small dependence on the total dose. Figure 3 shows the *G*-values of the four main products at the dose of 5×10^{20} eV cm^{-3} as functions of the concentration of methane. It is noticeable that the three nitrogeneous compounds, ammonia, hydrogen cyanide, and methyl azide, showed different dependences on the concentration of methane.

Table 1. The yield of formaldehyde produced by the hydrolysis of the polymer obtained in the γ-radiolysis of the liquid nitrogen solution of methane

Methane mol l^{-1}	Formaldehyde *G*
0.024	1.00
0.042	1.07
0.071	0.85
0.11	0.93
0.37	1.00
0.54	0.91

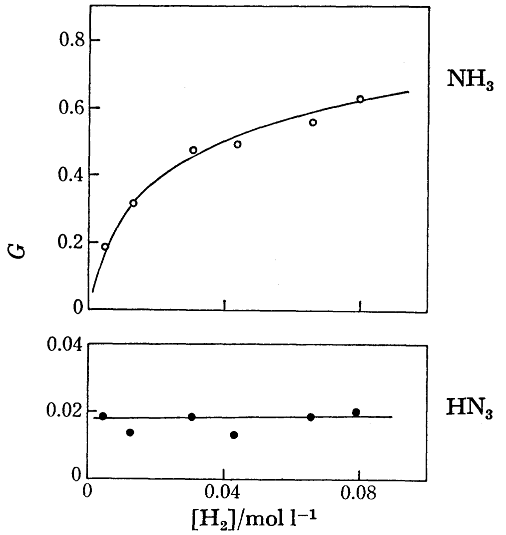

Fig. 1. *G*-Values of ammonia (○) and hydrogen azide (●) as functions of the concentration of hydrogen from the liquid nitrogen solution.

Table 1 shows the *G*-values of formaldehyde produced by the hydrolysis of the polymer. The *G*-values were about 1.0 in the concentration range from 0.02 to 0.5 mol l^{-1} of methane.

Ethane. Only volatile products were analyzed. The *G*-values of the main products at the dose of 5×10^{20} eV cm^{-3} are shown in Fig. 4 as functions of the concentration of ethane. The nitrogeneous compounds ob-

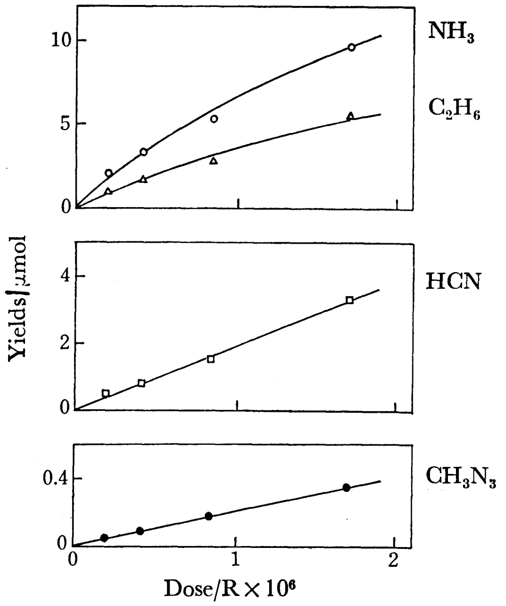

Fig. 2. The dose dependence of the yields of ammonia (○), ethane (△), hydrogen cyanide (□), and methyl azide (●) from the γ-radiolysis of a liquid nitrogen solution of 0.03 mol l^{-1} methane.

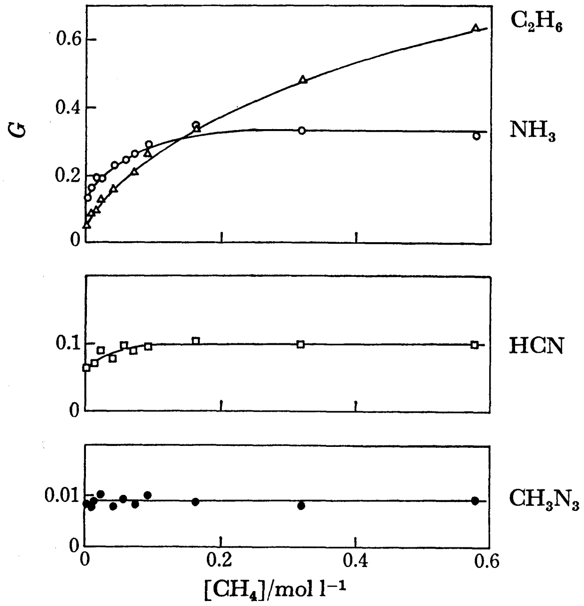

Fig. 3. *G*-Values of ammonia (○), ethane (△), hydrogen cyanide (□), and methyl azide (●) as functions of the concentration of methane from the liquid nitrogen solution.

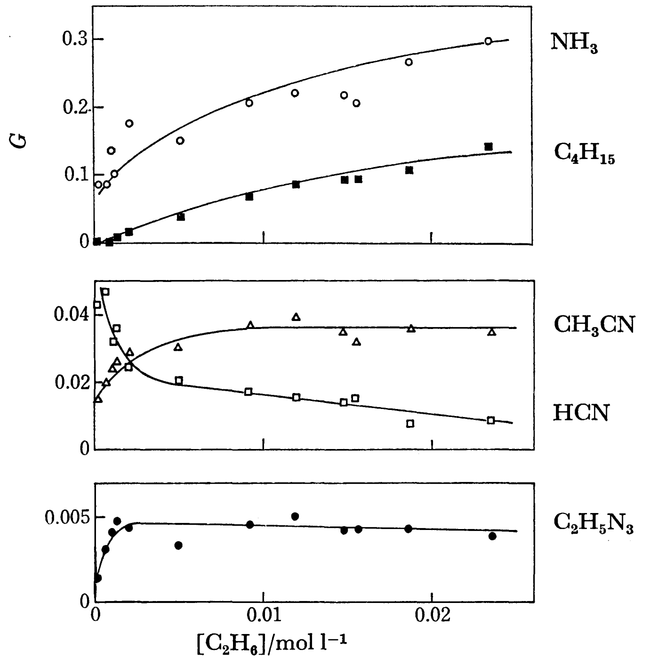

Fig. 4. G-Values of ammonia (○), butane (■), acetonitrile (△), hydrogen cyanide (□), and ethyl azide (●) as functions of the concentration of ethane from the liquid nitrogen solution.

served were ammonia, acetonitrile, hydrogen cyanide, and ethyl azide. The ethane concentration-dependence of the G-value of hydrogen cyanide was different from those of other products: *i.e.*, the G(HCN) decreased with increasing concentration of ethane. Repeated measurements showed the same dependence.

In the gas chromatographic analysis, the peaks of hydrogen azide and methyl azide overlapped with those of ethane and butane, respectively; therefore, the G-value of these two azides could not be measured.

Discussion

Formation of Ammonia. When ethylene was used as a solute, the formation of ammonia could not be observed in the gas chromatographic analysis.[8] As are shown in Figs. 1, 3, and 4, ammonia is one of the main products when hydrogen, methane, and ethane are used as solutes. This observation suggests that the presence of hydrogen atoms in the reacting system is indispensable for the formation of ammonia. Even at the temperature of liquid nitrogen, the addition reaction of hydrogen atoms to the double bond of olefins is a fast process.[9]

On the way to the formation of ammonia, the NH$_2$ radicals must be produced. If so, the formation of hydrazine, N$_2$H$_4$, can be expected; however, no hydrazine could be found even in the radiolysis of the liquid nitrogen–hydrogen system. Similarly, when methane or ethane is used as a solute, the formation of alkyl amines such as CH$_3$NH$_2$ and C$_2$H$_5$NH$_2$ can be expected; however, as stated in the Results section, no amines could be observed.

In order to explain these results, we tentatively considered the following reactions:

$$\mathrm{NH_2 + NH_2 \rightarrow NH_3 + NH,}$$
$$\mathrm{CH_3 + NH_2 \rightarrow CH_4 + NH,}$$
$$\mathrm{C_2H_5 + NH_2 \rightarrow C_2H_6 + NH,}$$
$$\mathrm{NH + NH \rightarrow N_2 + H_2.}$$

All of these reactions are exothermic by more than 10 kcal mol^{-1}. According to the measurement of Gillis,[10] the ratio of rate constants for disproportionation to combination of ethyl radicals at −181 °C is larger than four and the activation energy for combination exceeds that for disproportionation by about 300 cal mol^{-1}. Similar relations might also applicable to the reactions of NH$_2$ radicals and to the reactions between CH$_3$ and NH$_2$, and C$_2$H$_5$ and NH$_2$ radicals.

Formation of Nitrile Compounds. It is now well known that nitrogen atoms in the ground state, ^{4}S, are inactive to alkane molecules.[11] The formation of nitrogeneous compounds in the presence of alkane molecules, therefore, is due to the reactions of nitrogen atoms with alkyl radicals eventually formed in the system. However, the G-value of hydrogen cyanide obtained in the γ-radiolysis of the liquid nitrogen–methane system is only 0.1, as is shown in Fig. 3, a value which suggests that less than 10% of the nitrogen atoms are converted into nitrogeneous compounds. Consequently, as has been discussed in a previous paper,[5] we propose that the nitrile compounds observed in the gas chromatographic analysis are not the products of the reactions of nitrogen atoms in the ground state, ^{4}S, but those of nitrogen atoms in the excited state, ^{2}D.

$$\mathrm{CH_3 + N(^2D) \rightarrow HCN + H_2}$$
$$\mathrm{C_2H_5 + N(^2D) \rightarrow CH_3CN + H_2}$$

The presence of the excited state, ^{2}D, in the active nitrogen has been confirmed[12] and is known to have a long life. Moreover, if the nitrogen atoms are in the state of ^{4}S, the above reactions are not spin-allowed ones.

When ethane was used as a solute, the G-value of hydrogen cyanide decreased with increasing concentration of ethane. This decrease may be explained by the competition of nitrogen atoms (^{2}D) and ethylene, which is produced in the system, for methyl radicals. The formation of alkyl radicals and olefins may be described as follows:[3]

$$\mathrm{N_2(^3\Sigma_u{}^+) + CH_4 \rightarrow N_2 + CH_3 + H,}$$
$$\mathrm{N_2(^3\Sigma_u{}^+) + C_2H_6 \rightarrow N_2 + 2CH_3,}$$
$$\mathrm{\rightarrow N_2 + C_2H_5 + H,}$$
$$\mathrm{C_2H_5 + H \rightarrow C_2H_4 + H_2,}$$
$$\mathrm{\rightarrow C_2H_6.}$$

Formation of Polymer. As has been stated in the Results section, most of nitrogen atoms produced in the methane solution contribute to the formation of a polymer. The initiating reaction must be as follows:

$$\mathrm{CH_3 + N(^4S) \rightarrow CH_3N \rightarrow CH_2{=}NH.}$$

This type of imine is not stable at room temperature and easily polymerizes into a complex polymer.

According to the infrared spectroscopic study of the photolysis of methyl azide in a rigid matrix by Milligan,[13] methylimino radicals (CH$_3$N) produced in the photolysis of methyl azide isomerize to methylene imine in the matrix, and when the product is warmed up to temperatures where the matrix material is lost, a white solid is observed to remain on the wall. He measured the infrared spectrum of this solid and suggested that a part of it is hexamethylenetetramine.

We therefore looked for hexamethylenetetramine in our polymer by using gas chromatography, but we could not find it. Probably the main polymerization process is not the formation of this compound.

Formation of Azide. Because of the characteristic mass-spectra, the formation of azides was confirmed in the present experiment. As are shown in Figs. 1, 3, and 4, the *G*-values of all azides are not affected by concentrations of solutes in excess of 2×10^{-3} mol l^{-1}. If nitrogen atoms are the precursors of these azides, the yields should change with the concentration of solutes as do those of the ammonia and nitrile compounds. The N_3 radicals, therefore, may be produced by a process which is independent of the main process of the formation of nitrogen atoms—probably ion-molecule reactions, although we cannot specify them.

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