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The γ-Radiolysis of Liquid Nitrogen Containing Methane

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Synopsis. The γ-radiolysis of the liquid nitrogen-methane system has been investigated. As products, hydrogen cyanide, ethane, and the basic compounds were observed. The G(HCN) attained was 0.08 at higher concentrations of methane, while the G(basic compounds) was found to be in the order of 0.5. In order to explain these results, different precursors for the HCN and the basic compounds are considered.

Methane is the simplest hydrocarbon. Therefore, if γ-radiolysis is carried out with a system of liquid nitrogen containing a small amount of methane, the number of different products will be limited. In a study of the gas-phase γ-radiolysis of the nitrogen–methane system,1) it has been reported that hydrogen cyanide is the only nitrogen-containing product. Also, in an investigation of the reaction of the active nitrogen with methane,2) the main nitrogen-containing product has been found to be hydrogen cyanide.

At the temperature of liquid nitrogen, no reaction with an activation energy higher than a few kcal mol^{-1} will occur. Therefore, if the formation of hydrogen cyanide is accompanied by a complicated rearrangement, which is usually postulated in the gas-phase reactions of nitrogen atoms with hydrocarbons,3) these reactions will be inhibited in the liquid nitrogen; *i.e.*, only the association reaction and the strong exothermic reaction will occur.

With these expectations in mind, we have carried out the γ-radiolysis of liquid nitrogen containing methane.

Experimental

The methane used was supplied by the Takachiho Shoji Co. Nitrogen gas of a high purity was purchased from the Nihon Sanso Co. and was used after being bubbled through sulfuric acid. The hydrogen cyanide used for identification was synthesized from potassium cyanide and sulfuric acid. The Nessler reagent was obtained from Wako Pure Chemical Industries, Ltd.; sulfuric acid (95%) from the Yotsuhata Co., Ltd., and potassium carbonate, from the Junsei Pure Chemical Co., Ltd.

The experimental procedure was almost the same as that reported previously.4) A 10-ml portion of liquid nitrogen containing a known amount of methane was irradiated by ^{60}Co γ-rays at a dose rate of 3.21×10^{19} eV/g hr. After evacuating the nitrogen at 77 K, we analyzed the remains by using a gas chromatograph (DOP column) and by using Conway's method.4) The gas-chromatographic analysis showed the presence of hydrogen cyanide and ethane, while Conway's method revealed the presence of a comparatively large amount of the basic compounds in the product.

Results

Figure 1 shows the G-values of hydrogen cyanide and ethane obtained as functions of the concentration of methane. At methane concentrations higher than 3×10^{-3} mol l^{-1}, the increase in G(HCN) with an increase in the concentration of methane is much smaller than that in $G(C_2H_6)$. Table 1 summarizes the G-values of the basic compounds measured by Conway's method. Although the data are scattered, they may be enough to show that the G(basic compounds) is in the order of 0.5. One experiment was carried out using hydrogen in place of methane. This result suggests that the basic compounds obtained with methane are not products of the reaction of nitrogen atoms with the hydrogen eventually formed in the system.

Discussion

Since the C–H bond strength of methane (101 kcal

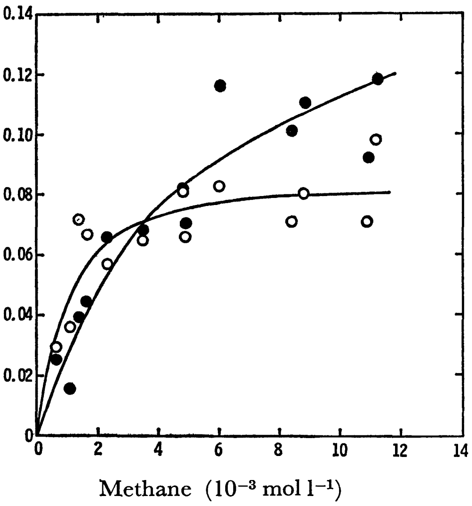

Fig. 1. The G-values of hydrogen cyanide (○) and ethane (●) as a function of the concentration of methane.

TABLE 1. THE G-VALUES OF AMMONIA MEASURED PHOTOMETRICALLY AFTER TREATING THE PRODUCT BY THE CONWAY METHOD AND USING NESSLER REAGENT

CH_4 (10^{-3} mol l^{-1})	H_2 (10^{-3} mol l^{-1})	$G(NH_3)$
0.56		0.44
1.29		0.36
2.01		0.60
2.83		0.51
3.57		0.41
	4.86	0.074

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mol^{-1}) is much larger than the bond strength of N–H (86 kcal mol^{-1}),[5] the endothermic reaction:

$$CH_4 + N \longrightarrow NH + CH_3 \qquad (1)$$

will not occur in the present system. The initiating reaction, therefore, must be the decomposition of methane in the collision of the excited nitrogen molecules with a long life ($N_2{}^*\ {}^3\Sigma_u{}^+$):

$$CH_4 + N_2{}^* \longrightarrow CH_3 + H + N_2 \qquad (2)$$

In the gas-phase reaction, the following reaction:

$$CH_3 + N \longrightarrow HCN + H_2 \qquad (3)$$

has often been assumed to occur; however, as was shown in the Results section, hydrogen cyanide is not the only nitrogen-containing product in the present experiment. Moreover, this reaction is not a spin-allowed one. A more plausible reaction in the present system is as follows:

$$CH_3 + N \longrightarrow CH_3N\colon \qquad (4)$$

The intermediate, CH_3N:, may isomerize into methylene imine either in the liquid nitrogen or in the course of the warming up to room temperature.

It is known that methylene imine is not a stable compound at room temperature and that it polymerizes into a polymer. In fact, the mass-spectrometric analysis of the product showed the presence of a polymer, although it could not be identified. If Reaction (4) is a unique reaction between nitrogen atoms and methyl radicals, the formation of hydrogen cyanide cannot be explained. Another possible mechanism is as follows:

$$CH_3 + N \longrightarrow H_2CN + H \qquad (5)$$

$$H_2CN + CH_3 \longrightarrow HCN + CH_4 \qquad (6)$$

Reaction (6) was proposed by Safrany and Jaster in the investigation of the reaction of active nitrogen.[5] However, this reaction mechanism is not applicable to the present system. As has been shown in Fig. 1, the methane-concentration dependence of G(HCN) is much smaller than that of $G(C_2H_6)$. If Reactions (5) and (6) are operative, the yield of hydrogen cyanide should be increased with the increase in the concentration of methyl radicals, which will itself increase with the concentration of methane.

As a possible source of hydrogen cyanide, let us consider the excited state of nitrogen atoms, ^2D, 2.38 eV above the ground state, ^4S. Even in the active nitrogen, the presence of the excited atoms ^2D has been reported, although the concentration is much less than that of the ground state.[3]

A tentative reaction mechanism to explain the present experimental results may be summarized as follows:

$$N_2 - \begin{cases} \rightsquigarrow 2\,N\ (^4S),\ (^2D) \\ \rightsquigarrow N_2{}^*\ (^3\Sigma_u{}^+) \end{cases}$$

$$N_2{}^* + CH_4 \longrightarrow N_2 + CH_3 + H$$

$$CH_3 + N\ (^2D) \longrightarrow HCN + H_2$$

$$CH_3 + N\ (^4S) \longrightarrow CH_3N\colon$$

$$CH_3N\colon \longrightarrow \text{products}$$

(Conway's method)

$$\text{products} \longrightarrow NH_3 + \text{residue}$$

$$CH_3 + CH_3 \longrightarrow C_2H_6$$

$$(H + N \longrightarrow NH \cdots\cdots\rightarrow NH_3)$$

Further investigations are being made with a different approach.

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References

1) A. T. Podkhalyuzin, A. E. Trishkin, and I. V. Vereshchinskii, *Khimiya Visokikh Energii*, **3**, 401 (1969). T. Oka, T. Shindo, and S. Sato, This Bulletin, **44**, 2274 (1971).

2) H. G. Evans, G. R. Freeman, and C. A. Winkler, *Can. J. Chem.*, **34**, 1271 (1956).

3) B. Brocklehurst and K. R Jennings, "Progress in Reaction Kinetics," Vol. 4, ed. by G. Porter, Pergamon Press, Oxford (1967), p. 1.

4) K. Ishizaki and S. Sato, This Bulletin, **47**, 2597 (1974).

5) D. R. Safrany, "Progress in Reaction Kinetics," Vol. 6, ed. by K. R. Jennings and R. B. Cundall, Pergamon Press, Oxford (1971), p. 1.