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The Radiolysis of Liquid Nitrogen Containing Hydrocarbons. I. Ethylene and Propylene

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The γ-radiolysis of liquid nitrogen containing ethylene and propylene has been investigated. As the nitrogenous products, hydrogen cyanide (0.18) and acetonitrile (0.04) were observed in the case of ethylene, and acetonitrile (0.12), in the case of propylene. The values in the parentheses are the G-values estimated on the basis of the energy absorbed by liquid nitrogen. In order to elucidate the mechanism of the reaction between nitrogen atoms and propylene, the mixture of C_3H_6 and C_3D_6 and the $CD_3CH=CHD$ compound have also been used as solutes. The acetonitrile obtained was mainly CH_3CN and CD_3CN in the former case, and CD_3CN in the latter. These results suggest that a nitrogen atom produced in the system attacks the carbon atom in the middle of propylene and produces acetonitrile, leaving a methyl radical, the carbon atom in which was originally attached to the double bond.

As an important branch of reaction kinetics, numerous investigations have been made of reactions between simple atoms and hydrocarbons.[1] Among them, the reaction between nitrogen atoms and hydrocarbons has been the most annoying one to investigators, because the reaction mechanism has to be formulated on the basis only of the measurement of a fragmentation product, hydrogen cyanide.[2] This compound is always observed as the principal product of the reaction between active nitrogen and hydrocarbons in the gas phase. Several researchers have reported that some other nitrogenous compounds, such as ammonia, acetonitrile,[3] and pyrrole,[4] are formed in the reaction between active nitrogen and hydrocarbons. However, the yields of these products are always too small compared with hydrogen cyanide to help to elucidate the reaction mechanism. Recently, though, Safrany and Jaster proposed a new approach to the reaction between active nitrogen and hydrocarbons;[5] they think that hydrogen cyanide obtained is not formed in the direct reaction between nitrogen atoms and hydrocarbons, but in the reaction between nitrogen atoms and the hydrocarbon radicals eventually formed in the reaction system.

With these things in mind, we have examined the γ-radiolysis of liquid nitrogen containing several hydrocarbons, and have found that hydrogen cyanide is not necessarily the principal nitrogenous product. For example, when propylene is used as the solute, the formation of hydrogen cyanide is not observed, but acetonitrile is formed. The

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[1] "Progress in Reaction Kinetics," Vols. 1, 2, 3 and 4 ed. by G. Porter, Pergamon Press, Oxford (1961—1967).

[2] G. G. Mannella, *Chem. Revs.*, **63**, 1 (1963).

[3] Y. Shinozaki, R. Shaw and N. N. Lichtin, *J. Am. Chem. Soc.*, **86**, 341 (1964).

[4] A. Tsukamoto and N. N. Lichtin, *ibid.*, **84**, 1601 (1962).

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

preliminary results with several hydrocarbons have been previously reported in a short communication.[6] These results suggest that the γ-radiolysis of a liquid nitrogen solution of hydrocarbons is a promising method for the study of the reactions between nitrogen atoms and hydrocarbons. In the present paper, we will report the details of the experimental method and procedure along with the results obtained with ethylene and propylene.

Experimental

Nitrogen gas of a high purity purchased from the Takachiho Trading Co. was bubbled through sulfuric acid before use. The gas-chromatographic analysis showed that the contamination of oxygen did not exceed 0.01%. All the hydrocarbons except the deuterated ones were of a pure grade purchased from the Takachiho Trading Co. The deuterated propylenes (C_3D_6 and $CD_3CH{=}CHD$) were synthesized from methylacetylene-d_4 by a method already reported.[7]

The vessel for γ-irradiation consisted of a simple Pyrex tube connected with a high-pressure stopcock through a joint held by a small spring. When the pressure in the tube rose over 2 atm, the spring was disengaged so as to avoid an explosion. The tube was graduated from the bottom in m*l*. To prepare the irradiation sample, a certain amount of a hydrocarbon volumetrically measured in advance was first condensed in the tube by means of liquid nitrogen. Then, nitrogen gas of a high purity was introduced under a pressure of about 1.5 atm. The gas was easily liquefied at the bottom of the tube. After a certain amount (usually 3 m*l*) of liquid nitrogen had been liquefied, the stopcock was closed and the tube was taken off the apparatus and shaken to dissolve the hydrocarbon in the liquid nitrogen. This sample tube was then irradiated with ^{60}Co-γ rays in a liquid-nitrogen Dewar flask. The exposure-dose rate used was 1.0×10^6 R/hr, and the irradiation time was usually 3 hr.

After the irradiation, the sample tube was evacuated at 77°K and the condensable product was analyzed by gas chromatography. For the analysis of acetonitrile, a 2.5-m column packed with polyethylene glycol-on-celite was used, while for hydrogen cyanide, a 2-m column of dioctyl phthalate was used. To detect the presence of ammonia, the irradiation product was treated with a Nessler reagent and the solution was analyzed spectrophotometrically at 430 mμ. The hydrocarbons were usually analyzed with a 4-m column of active alumina at a temperature of 40—60°C. To identify the nitriles, use was made of infrared and mass spectrometers.

TABLE 1. SOLUBILITIES OF ETHYLENE AND PROPYLENE IN LIQUID NITROGEN

Hydrocarbons	Solubility (mole fraction)
Ethylene	1×10^{-3}
Propylene	3×10^{-4}

Since the solubilities of hydrocarbons in liquid nitrogen could not be found in the literature, a rough estimate was made as follows. An excess amount of a hydrocarbon and a certain amount of liquid nitrogen were introduced into a sample tube which had a second thimble. After the ingredients had been mixed well, the solution was decantated into the second thimble, which was then evacuated at 77°K and fused. Then, the amount of the hydrocarbon remaining in the other thimble was measured volumetrically. Table 1 shows the results thus obtained. The numerical values should not be taken strictly, however.

Results

γ-Radiolysis of Liquid Nitrogen Containing Ethylene. The observed products were acetylene, hydrogen cyanide, acetonitrile, ethane, propane, *n*-butane, 1-butene, C_6-hydrocarbons, a trace of ammonia, and the polymer. Figure 1 shows the amount of hydrogen cyanide produced as a function of the irradiation time using two concentrations of ethylene. Figures 2 and 3 show the *G*-values

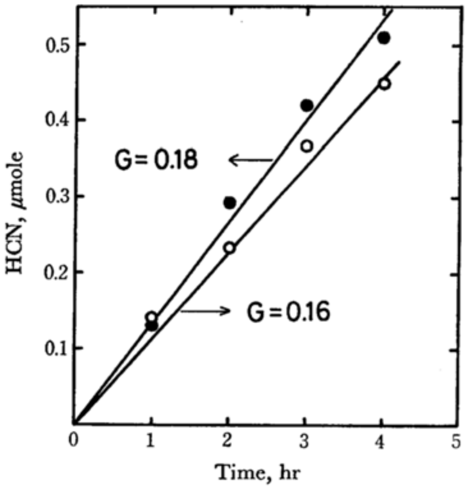

Fig. 1. Irradiation time dependence of HCN formation in ethylene-liquid nitrogen solution.

● C_2H_4, 2×10^{-4} in the mole fraction
○ C_2H_4, 1×10^{-4} in the mole fraction

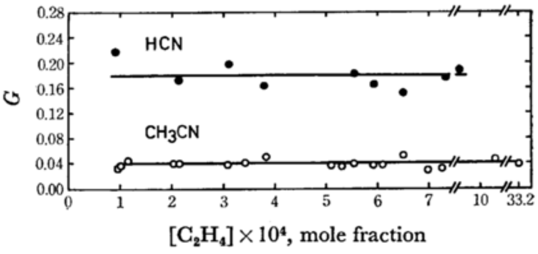

Fig. 2. *G*-values of CH_3CN and HCN from the ethylene-liquid nitrogen solution.

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[6] T. Oka and S. Sato, This Bulletin, **42**, 582 (1969).

[7] Y. Hatano, S. Shida and S. Sato, *ibid.*, **41**, 1120 (1968).

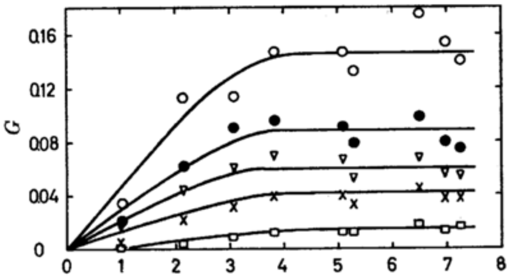

Fig. 3. G-values of hydrocarbon products from the ethylene-liquid nitrogen solution.

○ C_2H_6, ● $C_2H_2 \times 1/10$, ▽ C_3H_8, × n-C_4H_{10}, ☐ 1-C_4H_8.

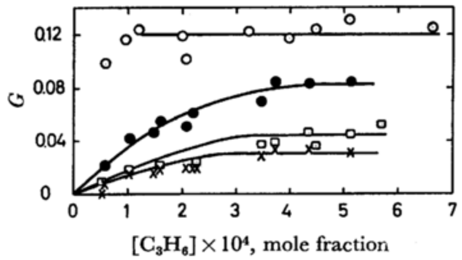

Fig. 5. G-values of products from the propylene-liquid nitrogen solution.

○ CH_3CN ● C_3H_8

☐ 4-methylpentene-1 and/or 2,3-dimethylbutane

× isobutane and/or allene.

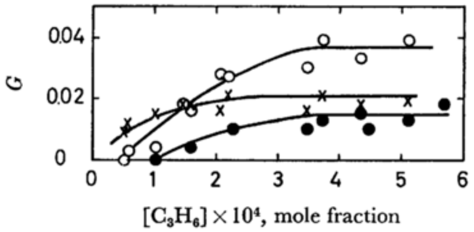

Fig. 6. G-values of products from the propylene-liquid nitrogen solution.

○ C_2H_4, × C_2H_6, ● 1,5-hexadiene.

TABLE 2. ISOTOPIC DISTRIBUTION OF ACETONITRILES PRODUCED IN THE γ-RADIOLYSIS OF LIQUID NITROGEN CONTAINING PROPYLENE

Propylene	Acetonitrile			
	d_3	d_2	d_1	d_0
$C_3H_6+C_3D_6$ (1:1)	72	15	8	100
$CD_3CH{=}CHD$	100	18	18	4

of the observed products as a function of the amount of ethylene introduced into the 3-m*l* portion of liquid nitrogen. The irradiation time was 3 hr at the dose rate of 1.0×10^6 R/hr. Obviously, nitrogenous products and hydrocarbons are different in their dependency upon the amount of ethylene introduced. The *G*-values of acetonitrile and hydrogen cyanide are practically constant over the range of mole fractions investigated, while the *G*-values of hydrocarbons increased initially and then leveled off over the mole fraction of 4×10^{-4}. When the liquid nitrogen was contaminated by oxygen, no products other than acetylene were observed and sometimes light emission and explosion occurred when the condensable product was warmed up for analysis.

γ-Radiolysis of Liquid Nitrogen Containing Propylene. The observed products were acetonitrile, propane, ethylene, ethane, isobutane and/or allene, 1,5-hexadiene, 4-methylpentene-1 and/or, 2,3-dimethylbutane, a trace of ammonia, and the polymer. The dose dependence of the formation of acetonitrile is shown in Fig. 4. The *G*-values of the observed products are shown in Figs. 5 and 6 as a function of the amount of propylene introduced. The dependences of the *G*-values of the products upon the amount of propylene are similar to those obtained with ethylene. Here, it should be noted that the formation of hydrogen cyanide is not observed.

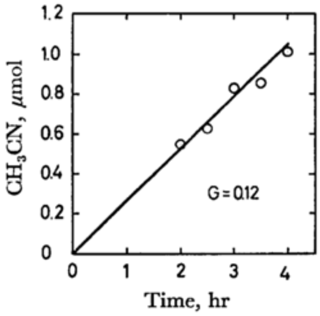

Fig. 4. Irradiation time dependence of CH_3CN formation in propylene-liquid nitrogen solution.

C_3H_6, 1.3×10^{-4} in the mole fraction

To elucidate the mechanism of the formation of acetonitrile, deuterated propylenes were used as solutes. Table 2 shows the distributions of the isotopic acetonitriles obtained with a partially-deuterated propylene ($CD_3CH{=}CHD$) and a 1 : 1 mixture of C_3H_6 and C_3D_6. Obviously, the main process of the formation of acetonitrile does not involve radical reactions. If it did, the d_1- and d_2-acetonitriles would be comparable in the amount with the d_0- and d_3-acetonitriles. The *G*-value of acetonitrile from a deuterated propylene solution was smaller than that from a usual propylene solution, although it was not measured quantitatively.

The Polymer Formation. Although the amount of the polymer formed was not measured in either radiolysis, its formation was detected as follows. After the analysis of the volatile products, the tube was heated in the air; thereby small black particles, probably carbon, were obtained on the inside wall.

Discussion

As has been stated above, ethylene and propylene are soluble in liquid nitrogen, although their amounts are very small. Moreover, as has been reported in a short communication,[6] hydrocarbons with high melting points gave no nitrogenous products.[*1] This is probably due to the small solubilities of these hydrocarbons in liquid nitrogen. From these facts, it may be concluded that the nitrogenous compounds observed are formed in homogeneous reactions in liquid nitrogen.

The initial reactions occurring in a γ-irradiated liquid nitrogen solution may be described as follows:

$$N_2 \rightsquigarrow [N_2^+ + e] \qquad (1)$$

$$\rightsquigarrow N_2^* \qquad (2)$$

$$\rightsquigarrow [N^+ + N + e] \qquad (3)$$

Here, brackets denote spurs. For the estimation of the G values of free ions, the $\exp(-r_c/r)$ factor is known to be important; it corresponds to the probability that a thermalized electron at the distance, r, from its parent positive ion can escape from the Coulombic field. Here, r_c stands for the Onsager length $(e^2/\varepsilon kT)$.[8] Since the dielectric constant of liquid nitrogen, ε, is close to 1.45, the Onsager length in liquid nitrogen is very much larger than that in a hydrocarbon liquid, for example, cyclohexane, at room temperature.[9] The G-values of free ions in cyclohexane are known to be about 0.1.[10] Therefore, the G values of free ions in liquid nitrogen will be much smaller than 0.1.

Since the concentration of the solute in the present experiment does not exceed 10^{-3} in the mole fraction, the reaction between the solute molecules and the ions in spurs may be ignored.[*2] In other words, almost all the electrons produced in the reactions (1) and (3) return to their respective ions and are neutralized, leaving an excited nitrogen molecule in the reaction (1) and two nitrogen atoms in the reaction (3).

In the gas-phase experiments, a long-lived excited state of the nitrogen molecule is known to be $N_2(A\ ^3\Sigma_u^+)$.[12] This excited state is not easily quenched by nitrogen molecules, and the life-time is estimated to be more than 10^{-2} sec. The active species responsible for the successive reactions in the liquid nitrogen solution, therefore, are probably nitrogen atoms and the excited molecules, $N_2(A\ ^3\Sigma_u^+)$. In many reports on the reactions of active nitrogen, it seems to have been established that the nitrogenous compounds observed are produced in the reaction of nitrogen atoms, but not in that of excited nitrogen molecules. Accordingly, the hydrogen cyanide and acetonitrile obtained in the present experiment may have been produced in the reactions of nitrogen atoms.

In the system of ethylene and liquid nitrogen, the formation of both hydrogen cyanide and acetonitrile has been observed. The reactions may be written as follows:

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

$$\searrow CH_3CN + H \qquad (5)$$

This mechanism contradicts that recently proposed by Safrany and Jaster.[5] According to them, hydrogen cyanide is mainly produced in the reaction between nitrogen atoms and such alkyl radicals as C_2H_5. However, the γ-radiolysis of the liquid nitrogen solution containing ethane gives more acetonitrile than hydrogen cyanide as the nitrogenous product.[13] This suggests that, even if it occurs, the reaction between ethyl radicals (this radical most probably exists in the present system) and nitrogen atoms gives mainly acetonitrile.

$$C_2H_5 + N \longrightarrow CH_3CN + H_2 \text{ (or 2H)} \qquad (6)$$

Reaction (5) has not been proposed in the gas-phase experiment. If ethyl radicals are produced in the system of ethylene and liquid nitrogen, as

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[*1] In the short communication, we have classified hydrocarbons into two groups, I and II. The group I involves ethylene, propylene, propane, allene, and 1-butene, which give nitrogenous products in the γ-radiolysis of the liquid nitrogen solution and which have melting points lower than −130°C, while those of the group II (acetylene, *trans*-2-butene, and 1,3-butadiene) do not give nitrogenous products and have melting points higher than the group I.

8) L. Onsager, *Phys. Rev.*, **54**, 554 (1938).

9) F. Williams, *J. Am. Chem. Soc.*, **86**, 3954 (1964).

10) W. F. Schmidt and A. O. Allen, *J. Phys. Chem.*, **72**, 3730 (1968).

[*2] The time taken for the geminate recombination after the ionization is estimated to be $10^{-10\pm1}$ sec.[9] On the other hand, the average time between two successive collisions of an ion A, with the solute, B, is estimated by means of this equation:[11]

$$t=\{4\pi(D_A+D_B)(R_A+R_B)n\}^{-1} \qquad (I)$$

Here, D is the diffusion constant, R is the collision radius, and n is the concentration of the solute, B. By assuming $D_{N_2^+}=10^{-5}$ cm²/sec, $D_{C_2H_4}=5.3\times10^{-5}$ cm²/sec, $R_{N_2^+}=2.4$ Å, $R_{C_2H_4}=1.9$ Å, and $t=10^{-10}$ sec, n is calculated to be 2.9×10^{20} molecules/cc, which corresponds to 1.7×10^{-2} in the mole fraction. This value is about 10^2 times the solute concentration in the present experiment.

11) N. V. Klassen, *ibid.*, **71**, 2409 (1967).

12) J. F. Noxon, *J. Chem. Phys.*, **36**, 926 (1962); H. B. Dunford, *J. Phys. Chem.*, **67**, 258 (1963).

13) T. Oka and S. Sato, to be published.

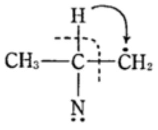
will be discussed later, the reaction (6) might be the only source of acetonitrile.

In the system of propylene and liquid nitrogen, the nitrogenous product was acetonitrile. The reaction may be written as follows:

$$\begin{array}{lll} C_3H_6 + N \longrightarrow & CH_3CN + CH_3 & (7) \\ \qquad\qquad\searrow & X \text{ (unknown)} & (8) \end{array}$$

The reaction (8) has to be involved because, in the case of ethylene, the total *G*-value of the nitrogenous products was 0.22, while that obtained with propylene was 0.12. The difference may be attributed to the formation of unknown products. A more thorough investigation of the products is obviously needed.

The results shown in Table 2 are very suggestive as to the details of the reaction (7). If the formation of acetonitrile is mainly due to the reaction between nitrogen atoms and some radicals, the acetonitrile obtained with the 1 : 1 mixture of C_3H_6 and C_3D_6 should contain many more d_1- and d_2-compounds than those shown in Table 2. Moreover, the results obtained with a partially-deuterated propylene ($CD_3CH{=}CHD$) clearly show that most of the methyl radical in propylene remains, as it is, in the acetonitrile produced. The bond cleavage in the intermediate, if it is produced, may be visualized as follows:



The reaction between nitrogen atoms and alkyl radicals, however, cannot be entirely ignored, because the formation of the d_1- and d_2- compounds has been observed with the 1 : 1 mixture.

In a previous note[14] on the γ-radiolysis of nitrogen gas, we have estimated the *G*-values of nitrogen atoms to be 0.8. This value is more than three times the *G*-value (0.22) of the nitrogenous products formed in the system of ethylene and liquid nitrogen. Since the cage effect has to be considered in the liquid, the value of 0.22 may not be far from the *G*-value of nitrogen atoms in liquid nitrogen.

The reaction of $N_2(A\ ^3\Sigma_u^+)$ with ethylene may be written as follows:[15]

$$N_2(A^3\Sigma_u^+) + C_2H_4 \longrightarrow N_2 + C_2H_4^*$$

$$\begin{array}{ll} C_2H_4^* \longrightarrow & C_2H_2 + H_2 \text{ (or 2H)} \\ \qquad\quad\searrow & C_2H_3 + H \end{array}$$

These reactions will be followed by such radical reactions as:

$$H + C_2H_4 \longrightarrow C_2H_5$$

$$C_2H_3 + C_2H_4 \longrightarrow C_4H_7$$

This is consistent with the finding that, in the presence of oxygen, the only product observed was acetylene. In the case of propylene, a similar reaction mechanism can easily be constructed.

The amount of each hydrocarbon observed in both radiolyses leveled off over the mole fraction of 4×10^{-4}. If this is due to the complete quenching of excited nitrogen molecules, the life-time of excited nitrogen molecules in liquid nitrogen can be estimated by using Eq. (I). The obtained value is about 10^{-8} sec. This is very much smaller than that estimated as the life-time in the gas phase. This is obviously another subject which needs to be investigated.

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

[15] D. D. Stedman, J. A. Meyer and D. W. Setser, *J. Am. Chem. Soc.*, **90**, 6856 (1968).