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The Radiolysis of Liquid Nitrogen Containing Hydrocarbons. III. Nitrile Formation from Solutions of Alkanes

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Recently, the radiolysis of liquid nitrogen containing simple olefins has been investigated in our laboratory in order to elucidate the mechanism of the reactions of nitrogen atoms with olefins.[1–3] In these studies, various nitrogenous compounds, such as hydrogen cyanide, acetonitrile, and propionitrile, were observed as products. The formation of these products was first attributed to the reactions of nitrogen atoms with olefins. However, a more detailed study showed that some of these products are formed by the reactions of alkyl radicals with nitrogen atoms.

In the study of the gas-phase reactions of active nitrogen with hydrocarbons, Safrany *et al.* showed that the reactions of nitrogen atoms with alkyl radicals do not produce nitriles, but hydrogen cyanide and ammonia.[4]

The present note will report the results of the radiolysis of liquid nitrogen containing simple alkanes and will discuss the mechanism of the formation of some of the nitrogenous products.

Experimental

Methane, ethane, and propane of a pure grade obtained from the Takachiho Trading Co. were used after bulb-to-bulb distillation. The samples were prepared and irradiated, and the products were analyzed as has been previously described.[2] Most of the samples were in ten-m*l* portions and were irradiated by ^{60}Co γ-rays for one hour at a dose rate of 0.9×10^6 R/hr.

Results

Propane. The observed products were acetonitrile, a trace of propionitrile, ethane, ethylene, isobutane, *n*-butane, 2,3-dimethylbutane and/or 2-methylpentane, *n*-hexane, an unspecified basic compound and a non-volatile product. Hydragen cyanide and propylene were not observed. All the volatile products increased linearly with the irradiation time up to two hours, the initial concentrations of propane used being 1×10^{-4} and 6×10^{-4} in the mole fraction. The *G*-values of acetonitrile and hexanes are shown in Fig. 1 as a function of the concentration of propane. The *G*-value of acetonitrile (0.08) seems to be independent of the concentration of propane, while those of the hexanes are dependent on it. This feature is similar to those observed when ethylene and propylene are used as solutes.[2,3]

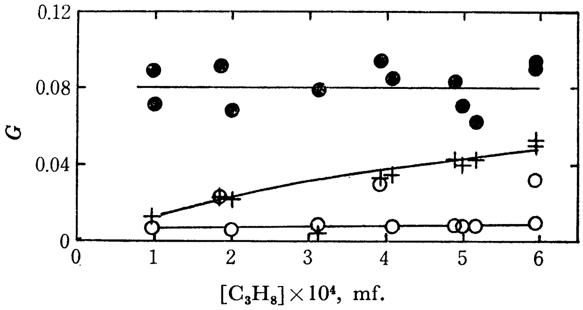

Fig. 1. *G*-values of acetonitrile (●), 2,3-dimethylbutane and/or 2-methylpentane (+) and *n*-hexane (○) as a function of the concentration of propane.

The presence of basic products was ascertained by the following method. After introducing hydrogen chloride onto a volatile product condensed at the temperature of liquid nitrogen, the system was warmed to room temperature. White particles were thus obtained. An aqueous solution of this solid was colored by the Nessler reagent. The non-volatile product was also soluble in water and was colored by the same reagent. The color observed for both solutions was similar to that when ammonium chloride was treated in the same manner. These three solutions showed similar absorption spectra in the region of 350 to 450 mμ. This result suggests that both volatile and non-volatile products contain basic nitrogenous compounds. However, they do not seem to be amines because ethyl and methyl amines have very weak absorptions in the wavelength region examined. Moreover, the volatile product is not simply ammonia, because the absorption at 430 mμ of the aqueous solu-

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1) T. Oka and S. Sato, This Bulletin, **42**, 582 (1969).
2) T. Oka, Y. Suda, and S. Sato, *ibid.*, **42**, 3083 (1969).
3) T. Oka and S. Sato, *ibid.*, **43**, 3711 (1970).
4) D. R. Safrany and W. Jaster, *J. Phys. Chem.*, **72**, 518 (1968).

tion increased gradually with the elapsed time for 30 min after preparation. Such a behavior cannot be observed with the solution of ammonium chloride. Every effort we have made hitherto has failed to identify these basic products.

Ethane. The observed products were acetonitrile ($G=0.025$), hydrogen cyanide ($G\sim0.001$), propane ($G\sim0.08$), acetylene ($G\sim0.01$), and *n*-butane ($G\sim0.04$). The basic products were not examined.

Methane. The nitrogenous product observed was hydrogen cyanide ($G=0.07$). The other products were not analyzed.

Discussion

In a study of the reactions of active nitrogen with alkanes, it was reported that nitrogen atoms in its ground state do not react with methane and ethane at room temperature.[4] The nitrogenous compounds observed in the present study, therefore, may not result from the reactions of nitrogen atoms in its ground state with alkanes. The following processes can be considered for the formation of nitrogenous compounds:

a) The reactions of nitrogen atoms in its ground state with alkyl radicals, which are eventually formed by the reactions of excited nitrogen molecules or nitrogen molecule ions with alkanes:

$$RH + N_2^* \rightarrow R\cdot + H + N_2$$

b) The reactions of electronically-excited nitrogen atoms(^{2}D) with alkane molecules, and

c) The reactions of nitrogen atoms with olefins of impurities or products.

Case c) can, though, be ruled out on the basis of the following facts; 1) In the cases of ethane and propane, propylene is not a product; if formed, it gives rise to acetonitrile in the reaction with nitrogen atoms.[2] 2) The acetonitrile observed in the case of propane was a primary product. 3) The propane used contained no propylene as an impurity.

Case b) cannot be denied by the experimental facts. However, N(^{2}D) can be expected to form ammonia or amines rather than cyanides in reactions with alkanes, judging from the reactions of O(^{1}D),[5] S(^{1}D),[6] C(^{1}S),[7] and nitrene[8] with alkanes.

Case a), which is most likely, can explain the experimental results as follows; if the most abundant alkyl radicals are taken account of in each system, in the case of methane:

$$CH_3 + N \rightarrow HCN + 2H, \qquad (1)$$

in the case of ethane:

$$C_2H_5 + N \rightarrow CH_3CN + 2H, \qquad (2)$$

and in the case of propane:

$$iso\text{-}C_3H_7 + N \rightarrow CH_3CN + CH_3 + H. \qquad (3)$$

These reactions have already been proposed to explain the formation of a part of the cyanides obtained in the radiolysis of liquid nitrogen containing olefins.[2-3] In the gas phase, it was suggested by Safrany and Jaster that these reactions produce HCN or NH.[4] This apparent disagreement may be due to the difference in deactivation.

The basic products observed might be imines, whose formation has been suggested in the thermolysis and photolysis of methylazide.[8] Obviously, further investigations are needed.

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[6] a) A. R. Knight, O. P. Strausz, and H. E. Gunning, *J. Amer. Chem. Soc.*, **85**, 2349 (1963). b) K. Gollnick and E. Leppin, *ibid.*, **92**, 2217 (1970).

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