A New Approach to the Study of the Reactions of Nitrogen Atoms with Hydrocarbons

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The reactions of nitrogen atoms with various hydrocarbons have been extensively investigated by many investigators using the discharge of nitrogen gas at low pressures.[1-4] The main product observed in their experiments was hydrogen cyanide. Other products, such as ammonia and methyl cyanide, were always found in minor amounts.

Recently, a few groups, including that of our laboratory, used high-energy radiations to produce nitrogen atoms in the gas phase at higher pressures.[5] However, nitrogen-containing product observed was again only hydrogen cyanide, and the reaction mechanism was very much complicated by the participation of nitrogen molecule ions in the reactions.

We have studied the γ-radiolysis of a liquid nitrogen containing small amounts of various hydrocarbons. This short communication will report the preliminary results obtained; these results are quite different from the results obtained in the gas phase.[5]

When a 3-m*l* portion of liquid nitrogen containing 4×10^{-2} mol% of propylene was irradiated at 77°K by γ-rays for three hours at the dose rate of 10^6 R/hr, the products observed were methyl cyanide (0.80 μmol), propane (0.55 μmol), and small amounts of ethane, ethylene, isobutane, 4-methylpentene-1 and ammonia. The absence of hydrogen cyanide was noticeable.

Table 1 summarizes the results for nitrogen-containing products obtained when various hydrocarbons were used. With the hydrocarbons of group 1, various nitrogen-containing products were observed, while with those of group 2 practically no such products were observed. At first sight, this appears to indicate that nitrogen atoms have less reactivity to the hydrocarbons in the group 2.

Table 1. Nitrogen containing products and their approximate *G*-values[a]

Hydrocarbon[b]	Products (*G*-values)	Mp °C
	Group I	
Ethylene	HCN (0.2), CH_3CN (0.1), NH_3 (small)[c]	−169.2
Propane	CH_3CN (0.08)	−189.9
Propylene	CH_3CN (0.13), NH_3 (small)[c]	−185.2
Allene	HCN (small), CH_3CN (0.05), CH_2=CHCN (0.05)	−136.0
Butene-1	HCN (small), CH_3CN (0.05), C_2H_5CN (0.05)	−185.4
	Group II	
Acetylene	no HCN	−81.8
trans-Butene-2	no HCN, no nitril compounds	−105.6
1,3-Butadiene	HCN (small), no nitril compounds	−108.9

a) Estimations are based on the energy absorbed by liquid nitrogen.
b) Mole fraction of each hydrocarbon is in the order of 10^{-4}.
c) After treated with Nessler reagent, analyzed spectrophotometrically at 430 mμ.

However, it may be expected from the melting points listed in the table that the hydrocarbons of the group 1 are more soluble in liquid nitrogen than are those of the group 2. This may be the reason why the hydrocarbons of the group 2 give few nitrogen-containing products.

Experimental. A certain amount of hydrocarbon was frozen in a sample tube at 77°K. When compressed nitrogen gas (1.5 atm) was then introduced into the tube at 77°K, nitrogen was gradually liquefied at the bottom of the tube. This was continued until a required volume of the liquid was obtained. Then the cock of the tube was closed and the tube was removed from the vacuum line. The sample was then vigorously shaken in order to mix its contents. After irradiation, the volatile components were pumped off from the mixture at 77°K and the residue was analyzed by gas chromatography (a 5-m column packed with Carbowax 20 M and a 2-m column of dioctyl phthalate), mass spectrometry, and infrared spectroscopy.

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