The Cyanation of Ethylene with Cyanogen by a Silent Discharge

Tomiya ISSHIKI,*1 Noboru SONODA and Shigeru TSUTSUMI

Department of Chemical Technology, Faculty of Engineering, Osaka University, Yamadakami, Suita, Osaka

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There have been several patents[1-3] on the reaction of cyanogen with olefins. It has been shown that the reaction of cyanogen with ethylene over a nichrome wire coil above 815°C gives rise to succinonitrile,[1] whereas in the absence of a catalyst acrylonitrile was produced at 750—900°C,[2] or at 300—700°C under low pressure.[3] These facts show that the reaction of cyanogen with olefin may require high temperatures because of the high activation energy. In connection with our study on the reaction under an electrical discharge, a similar reaction was undertaken in a silent discharge, which seemed to resemble a high LET radiation process.[4] It was observed that the reaction proceeded smoothly at room temperature under atmospheric pressure.

The reaction of equimolar amounts of cyanogen and ethylene gave acrylonitrile as the main product in a yield of 40.0%, based on unrecovered ethylene, and propionitrile and valeronitrile were also formed in yields of 5.3 and 9.5%, respectively. A trace amount of adiponitrile was detected, and some undetectable solid, deposited on the surface of the discharge tube, was obtained. The gaseous products indentified were acetylene (7.6%), ethane (1.9%) and small amounts of butane, 1-butene, methane, hydrogen cyanide and hydrogen.

It was reported that acetylene was the main product of a silent discharge reaction with ethylene,[5] and that the reaction of cyanogen[6] in a silent discharge would give cyanoradical as an intermediate. Although little information was obtained about the reaction mechanism in the present experiment, acetylene may not be the precursor of acrylonitrile, because the addition of a small amount of acetylene to the reaction mixture did not cause any increase in the yield of the cyanated products.

Experimental

The silent discharge tube used was a Siemens type tube made of hard glass; discharge length, 24 cm; space gap, 3.5 mm; discharge space volume, 50 m*l*. The secondary voltage applied was 15 kV, and secondary current 1.0 mA at 60 cycles.

A gaseous mixture of 25.3 *l* of ethylene (0.503 mol) and cyanogen (0.503 mol) was circulated at the rate of 1.4 *l* min through the Siemens tube, and the effluent gas, before returning to the gas container, was passed through a cold trap at −20°C to collect condensable products.

After the discharge was continued for 7 hr, the components of the gaseous products were analyzed by v. p. c. using columns of activated charcoal and tricresyl phosphate: ethylene (0.293 mol), cyanogen (0.394 mol), acetylene (0.016 mol), ethane (0.004 mol), methane (0.001 mol), and trace amounts of 1-butene, butane, hydrogen, hydrogen cyanide and acrylonitrile were detected. To the condensed liquid products (8.2 g) was added a small amount of hydroquinone to prevent the polymerization of unsaturated products, and the resulting mixture was distilled under reduced pressure in a nitrogen atmosphere to give 5.7 g of a fraction boiling at 110°C/7 mmHg and 2.4 g of residue. Vapor phase chromatographic analysis of the fraction and the residue using a tricresyl phosphate column showed the presence of acrylonitrile (4.5 g), propionitrile (0.6 g), valeronitrile (0.8 g), adiponitrile (trace) and a small amount of unidentified products.

The acrylonitrile formed was also confirmed as its dibromo derivative; bromination of the liquid sample boiling at 76—78°C, obtained by redistillation of the above fraction, gave 2,3-dibromopropionitrile, which was identified by elementary analysis and the complete coincidence of the infrared spectrum with that of an authentic sample.

Found: C, 16.82; H, 1.56; N, 6.49; Br, 75.00%. Calcd for $C_3H_3NBr_2$: C, 16.93; H, 1.42; N, 6.58; Br, 75.04%.

*1 Inquiries should be addressed to: Research Institute, Mitsubishi Edogawa Chemical Co., Ltd., 6-3 Chome, Kanda, Surugadai, Chiyoda-ku, Tokyo.

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