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The Reaction between Hydrocarbon and Hydrogen Cyanide in Silent Electrical Discharge. II.[1] The Formation of Acrylonitrile from Ethylene and Hydrogen Cyanide*1

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The present investigation was undertaken to examine the possibility of the direct introduction of a cyano radical into ethylene by means of a silent discharge. When a mixture of ethylene and hydrogen cyanide was discharged in an ozonizer under atmospheric pressure, the main liquid product was acrylonitrile, though the formation of telomers, such as ethyl cyanide, *n*-butyl cyanide and *n*-hexyl cyanide, was also observed. Besides these compounds, the reaction products were confirmed to consist of *s*-butyl, *n*-propyl, isopropyl, *n*-amyl, and isoamyl cyanides, and a gaseous product. The yield of acrylonitrile was affected by the temperature and voltage of the discharge. It has been found that the yields of the liquid products and the gaseous product increase with the rise in the temperature and voltage of the discharge, while the relative ratio of acrylonitrile to the other liquid product decreases. Judging from the relative concentration of each compound in the reaction products, it may be said that the vinyl radical and the cyano radical are the main intermediates in this reaction system.

Studies concerning the reaction of ethylene alone in electrical discharge have been reported by many investigators.[2] Moreover, in recent years, the reactions of ethylene and ammonia or oxygen under silent electrical discharge have been investigated by Sugino *et al.*[3] and by Tsutsumi *et al.*[4]

In a previous study,[1] it was found that, when a mixture of cyclohexane and hydrogen cyanide was discharged in an ozonizer, cyclohexyl cyanide could be prepared in one step, and that the relative amounts of this compound depended not only upon the discharge voltage, but also upon the discharge temperature.

The direct synthesis of acrylonitrile from ethylene and cyano-compounds has been established in several patents. (1) Acrylonitrile was obtained by the addition of cyanogen chloride or cyanogen bromide to ethylene in the presence of $AlCl_3$ and CH_3NO_2.[5] (2) It was found by Oberbacher[6] that

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[1] K. Kawamoto, N. Sonoda and S. Tsutsumi, This Bulletin, **41**, 1376 (1968).

[*1] The results of this investigation were presented at the 18th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1965; some of them were also presented at the 19th Annual Meeting of the Chemical Society of Japan, Yokohama, April, 1966.

[2] These reports are summarized by C. L. Thomas, G. Egloff and J. C. Morell, *Chem. Revs.*, **28**, 1 (1941).

[3] T. Matsuda, K. Oto and K. Sugino, *Nippon Kagaku Zasshi* (*J. Chem. Soc. Japan, Pure Chem. Sect.*), **79**, 325 (1958); K. Sugino, E. Inoue, K. Shirai, T. Koseki and T. Gomi, *ibid.*, **86**, 114 (1965).

[4] S. Yamamoto, N. Sonoda and S. Tsutsumi, Preprints for of the 17th Annual Meeting of the Chemical Society of Japan, (April, 1964), p. 24.

[5] Brit. Pat. 686692; *Chem. Abstr.*, **48**, 8251 (1954).

[6] B. Oberbacher, German Pat. 1034625; *Chem. Abstr.*, **54**, 11996 (1960).

acrylonitrile could be prepared by the reaction of ethylene with cyanogen at 300—700°C at low pressures. (3) Porter and Nesty[7] and Sandner and Fierce[8] found that, in the absence of a catalyst, when ethylene was reacted with cyanogen or hydrogen cyanide at about 750—900°C it was transformed into acrylonitrile.

Francesconi and Ciurlo[9] reported that when a mixture of ethylene and hydrogen cyanide was subjected to the electrical discharge, ethyl cyanide and ethyl isocyanide were obtained.

In the present paper, the author wishes to report the direct formation of acrylonitrile in a reaction between ethylene and hydrogen cyanide in a silent discharge, and to establish, if possible, the most suitable conditions for the formation of acrylonitrile.

Experimental

Materials. The ethylene used in this experiment showed no impurity in gas-chromatographic analysis. (Columns of activated charcoal and dimethyl sulfolane were used.) The hydrogen cyanide was prepared according to Brauer's method.[10]

Apparatus and Procedure. The apparatus employed was similar to that used by the passing method in the previous paper.[1] The discharge tube used was a Pyrex tube 40 cm in effective length, 4 cm in outside diameter, and with a space gap of 0.25 cm. Ethylene and hydrogen cyanide vapor were passed through the discharge tube at a constant velocity for the period of the reaction. The amount of hydrogen cyanide used in each experiment was about a 2-mol. A 60-cycle alternating current was sent through a voltage regulator, and the voltage was stepped up by a transformer (Capacity: 15 kV) to give the required value. The products coming out of the discharge tube were removed by being passed through a condenser cooled with ice water, supplemented by two traps which were cooled with ice. The liquid products were analyzed by the method described below, while the noncondensable gas was analyzed by gas chromatography at intervals of 30 min.

Identification and Analysis of the Reaction Products. The reaction products were identified by comparing them with the authentic samples[*2] by gas chromatography. (Columns of tricresyl phosphate, PEG-6000, and silicone DC 550 were used.) In addition, the reaction products were fractionally distilled in the presence of a small amount of hydroquinone, and the constituents of the cut were identified by the formation of the derivatives described below and by the infrared absorption.

The fraction boiling at 75—79°C was confirmed to consist mainly of acrylonitrile by transforming it into the *N*-*t*-butyl acrylamide,[*3] mp 126—128°C, and the picrate of β-piperidinopropionitirle, [*4] mp 160—161°C. They showed no depression in their melting points when mixed with authentic specimens. The infrared spectrum of this fraction agreed with that of authentic acrylonitrile. Besides acrylonitrile, the reaction products were identified by the methods described below.[*5]

The gaseous products, when analyzed by gas chromatography, were found to consist of ethane, acetylene, hydrogen, *n*-butane, 1-butene, 1,3-butadiene, methane, propane, and propylene. (Columns of activated charcoal, tricresyl phosphate, acetonylacetone, and dimethyl sulfolane were used.) The gaseous products could not be determined quantitatively. The liquid products were analyzed quantitatively by gas chromatography using a 5-m column of PEG-6000, a 3-m column of silicone DC 550, and a 3-m column of tricresyl phosphate at 140°C. Further, the content of acrylonitrile was also determined by the method of Beesing *et al.*[11] However, the difference between this method and gas-chromatographic analysis was less than 2 per cent.

Results and Discussion

By running ethylene with hydrogen cyanide only one time in an ozonizer under the conditions described in Table 1, a large number of compounds were obtained, along with acrylonitrile as the object substance. Among these, the identified compounds are summarized in Table 2. The compositions of the reaction products given in this table are reproducible within 1 per cent. In the presence of a small quantity of air, a solid brown deposit was formed on the glass wall. Accordingly, the air was completely removed from the reaction system. The liquid product absorbed oxygen from the air quite readily, and it was polymerized upon standing at room temperature.

Influences of the Discharge Temperatures and Voltages on the Reaction between Ethylene and Hydrogen Cyanide. As may be seen from

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7) F. Porter and G. A. Nesty, U. S. Pat. 2445693; *Chem. Abstr.*, **42**, 8209 (1948).

8) W. J. Sandner and W. L. Fierce, U. S. Pat. 2803641; *Chem. Abstr.*, **52**, 5449 (1958).

9) L. Francesconi and A. Ciurlo, *Gazz. Chim. Ital.*, **53**, 327 (1923).

10) G. Brauer, " Handbuch der Präparativen Anorganischen Chemie, " Ferdinand Enke Verlag, Stuttgart (1954), p. 500.

[*2] *s*-Butyl, isoamyl, *n*-amyl, and *n*-hexyl cyanides were prepared according to the procedure of Jeffery and Vogel; G. H. Jeffery and A. I. Vogel, *J. Chem. Soc.*, **1948**, 679. Further, the following commercial chemicals were used for identification: acrylonitrile, ethyl cyanide, *n*-propyl cyanide, isopropyl cyanide and *n*-butyl cyanide.

[*3] *N*-*t*-Butyl acrylamide was prepared according to the procedure of Plaut and Ritter; H. Plaut and J. J. Ritter, *J. Am. Chem. Soc.*, **73**, 4076 (1951).

[*4] The picrate of β-piperidinopropionitrile was prepared by Brockway's method; C. E. Brockway, *Anal. Chem.*, **21**, 1207 (1949).

[*5] (1) Ethyl cyanide was present in a fraction boiling at 92—97°C, and the ethyl 2,4,6-trihydroxyphenyl ketone, mp 175—176°C, was obtained. (2) *n*-Butyl cyanide was present in the fraction distilling at 136—141°C; this compound gave the *n*-butyl 2,4,6-trihydroxyphenyl ketone, mp 87—88°C. These alkyl (2,4,6-trihydroxyphenyl) ketones were prepared by the procedure of Howells and Little; H. P. Howells and J. G. Little, *J. Am. Chem. Soc.*, **54**, 2451 (1932). The infrared spectrum showed a strong absorption band at 2250 cm^{-1} ($C\equiv N$). (3) The other products were identified by comparing their retention times on the gas chromatography with those of authentic compounds.

11) D. W. Beesing, W. P. Tyler, D. M. Kurty and S. A. Harrison, *Anal. Chem.*, **21**, 1073 (1949).

Table 1. The reaction between ethylene and hydrogen cyanide in silent electrical discharge (Experimental conditions)

Experiment No.	1	2	3	4	5
Ethylene used, *l*	22.17	22.67	27.59	27.54	27.69
Velocity, *l*/hr	3.70	3.78	3.07	3.06	3.08
Discharge time, hr	6	6	9	9	9
Second. voltage, kV	13	13	12	13.5	15
Second. current, mA	1.8	1.8	1.7	1.9	2.1
Temp. of discharge tube					
Inside, °C	30—67	10—26	10—26	10—26	10—26
Outside, °C	30—60	10	10	10	10

Table 2. The reaction between ethylene and hydrogen cyanide in silent electrical discharge (Experimental results)

Experiment No.	1	2	3	4	5
Liquid product collected, g	31.28	33.12	35.41	35.62	34.09
Reaction product, g	4.59	3.25	4.44	5.21	6.47
Conversion efficiency,[*1] %	16.5	11.4	12.8	15.1	18.6
Composition of liquid reaction products[*2]					
Acrylonitrile, %	45.8	57.9	59.9	52.1	45.9
Ethyl cyanide, %	12.6	7.1	7.0	9.2	12.9
n-Butyl cyanide, %	17.2	12.6	11.4	15.2	17.1
s-Butyl cyanide, %	10.6	6.7	5.9	8.0	10.2
n-Propyl cyanide, %	2.6	2.8	2.5	2.9	2.9
Isopropyl cyanide, %	2.0	1.9	1.8	1.7	2.0
n-Hexyl cyanide, %	T	T	T	T	T
n-Amyl cyanide, %	T	T	T	T	T
Isoamyl cyanide, %	T	T	T	T	T
Unidentified product, %	9.2	11.0	11.5	10.9	9.0

[*1] The conversion efficiency was given by (grams of reaction product/grams of ethylene used) × 100.

[*2] The yields of each compound produced were given by (grams of each compound/grams of total reaction product) × 100.

T: Trace

Experiments Nos. 1 and 2 in Table 2, the conversion efficiency (grams of reaction product/grams of ethylene used × 100) depends upon the temperature at which the discharge is carried out; it has been found that the yields of the liquid product and the gaseous product increase with a rise in the discharge temperature, and that, further, in the case of a high-temperature discharge, the proportion of acrylonitrile in the liquid product decreases and the yeilds of ethyl cyanide, *n*-butyl cyanide, and *s*-butyl cyanide increase. Thus, it may be said that a low temperature favors the formation of acrylonitrile. Ethyl, *n*-butyl, and *n*-hexyl cyanides seem to be formed by the telomerization between ethylene and hydrogen cyanide. However, the formation of *n*-octyl cyanide (1 : 4 telomer) and one-to-five or more products could not be observed by gas-chromatographic analysis. Further, the author could not find any dicyano-compounds and isocyano-compounds in the present research.

As may be seen from Experiments Nos. 3, 4 and 5 in Table 2, the yield of the reaction product was also affected by the discharge voltage; it has been found that increasing the voltage increases the yields of the liquid product and the gaseous product. Thus, the amount of ethylene reacted was at a maximum at the maximum voltage used in this experiment.

The Mechanism of the Formation of Acrylonitrile. It was reported by Egloff *et al.*2) that the radical from ethylene in the electrical discharge was a vinyl radical, and that it was produced by breaking a carbon-hydrogen bond. Tsutsumi12) reported that the vinyl radical was obtained by two molecular processes,[*6] as is shown below.

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12) S. Tsutsumi, *Chem. Ind.* (*Kagaku Kogyo*), **16**, 623 (1965).

[*6] $CH_2{=}CH_2 + e^* \rightarrow CH_2{=}CH_2^* + e$

$CH_2{=}CH_2^* + CH_2{=}CH_2 \rightarrow$

$CH_2{=}\dot{C}H + CH_3\text{-}\dot{C}H_2$

The formation of acrylonitrile by the reaction of ethylene with hydrogen cyanide in a silent discharge may be represented as follows: The first step is the activation of the ethylene molecule and the hydrogen cyanide molecule by electron impact, while the second step consists of both (1) the reaction of the activated ethylene molecule with a normal ethylene molecule to give the vinyl radical and the ethyl radical, and (2) the decomposition of the activated molecules to give the vinyl radical, the cyano radical, and the hydrogen atom. Acrylonitrile may be formed by a combination of the vinyl radical and the cyano radical thus obtained. Further, the formation of acetylene, 1,3-butadiene, and 1-butene may show the existence of the vinyl radical.

The Reaction Occurring in the Silent Discharge. Although the reaction of ethylene with hydrogen cyanide in a silent discharge is somewhat complicated by a secondary reaction, the principal reaction can be interpreted as including the formation of the vinyl radical, the ethyl radical, the cyano radical, and the hydrogen atom and the combination of these radicals, telomerization, hydrogenation, and dehydrogenation.

Besides acrylonitrile, considerable quantities of one-to-one products and one-to-two products, such as ethyl cyanide and *n*-butyl cyanide, were produced. Since the investigated reaction is presumed to be a radical reaction, the mechanisms of these telomers may be described as below:

$$HCN + e^* \rightarrow HCN^* + e \rightarrow \cdot H + \cdot CN \quad (1)$$

$$CH_2{=}CH_2 + \cdot CN \rightarrow \cdot CH_2CH_2CN \quad (2)$$

$$\cdot CH_2CH_2CN + HCN \rightarrow CH_3CH_2CN + \cdot CN \quad (3)$$

$$\cdot CH_2CH_2CN + CH_2{=}CH_2 \rightarrow \cdot CH_2(CH_2)_3CN \quad (4)$$

$$\cdot CH_2(CH_2)_3CN + HCN \rightarrow CH_3(CH_2)_3CN + \cdot CN \quad (5)$$

$$\cdot CH_2(CH_2)_3CN + CH_2{=}CH_2 \rightarrow \cdot CH_2(CH_2)_5CN \quad (6)$$

$$\cdot CH_2(CH_2)_5CN + HCN \rightarrow CH_3(CH_2)_5CN + \cdot CN \quad (7)$$

The addition reaction of the $C_6H_{12}CN$ radical to ethylene in these reaction mechanisms need not be considered, since no products beyond *n*-hexyl cyanide were obtained. In addition, a part of the ethyl cyanide may be formed by the reaction between the ethyl radical obtained by two molecular processes[*6] and the cyano radical. Further, it seems that ethane, *n*-butane, and 1-butene are obtained by the ethyl radical.

Beer and Besprozvannyi[13)] found, from their data on the telomerization of ethylene in carbon tetrachloride and chloroform, that compounds ($ClCH_2(CH_2)_3CCl_3$ and $CH_3(CH_2)_3CCl_3$) with $n=2$ were formed over a wide range of ethylene concentration. They suggested that the predominance of telomers with $n=2$ resulted from the stabilization of the trichloroamyl radical by a " pseudo cyclic " configuration between the unpaired electron of the end CH_2 and the electrophilic CCl_3 groups. As may be seen from Table 2, the yield of the telomer (*n*-butyl cyanide) with $n=2$ was higher than that of the telomer (*n*-hexyl cyanide) with $n=3$. Accordingly, the existence of a pseudo cyclic arrangement may be supported in the reaction of ethylene with hydrogen cyanide under a silent discharge. The formation of *s*-butyl cyanide was also observed. This is presumably due to the isomerization of *n*-butyl cyanide to *s*-butyl cyanide.

The author wishes to express his hearty thanks to Professor S. Tsutsumi of Osaka University for his kind guidance and valuable suggestions throughout this work.

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13) A. A. Beer and M. A. Besprozvannyi, *Khim. Nauka i Prom.*, **4**, 547 (1959).