

## Synthesis of Acrylonitrile

Kazuaki KAWAMOTO and Keiko TAMURA

Acrylonitrile is a very important chemical intermediate for various plastics. As a copolymer with 1,3-butadiene, it gives the so-called Buna N rubber. This material is particularly resistant to attack by hydrocarbon solvents and is therefore frequently used where the rubber might come in contact with gasoline or oils. The rubber found very important commercial application during the war of 1939-1945.

Acrylonitrile polymerizes readily to give linear polymers having fiber forming characteristics. In the case of Japan, acrylic fibers are sold under the trade names "Beslon", "Cashmilon", "Exlan", "Kanealon", "Torelon", and "Vonnell". The small proportion of foreign monomer (methyl acrylate or vinyl chloride) added to the acrylonitrile varies in character. The additives confer on the fiber greater chemical resistance, greater strength or improved dyeing characteristics.† Acrylic fibers possess lightness, resistance to sunlight, springiness and bulkiness which can be increased by super drawing, are water resistant and quick drying, and are similar to wool in many respects. Their resistance to abrasion is greater than that of wool but not as great as Nylon and polyesters. Acrylic fibers are resistant, even to concentrated acids except nitric acid and to weak alkali. Furthermore, these fibers are unaffected by common solvents, and by mildew or moths. The remarkable characteristics of these fibers are their softness of handle and crease recovery. The end uses for acrylic fibers comprise sweaters, underwear, women's

coats, men's winter suitings, carpets, high bulk knitwear, fleecy linings and blankets. Blends of acrylics with wool are used for suitings, dress goods and knitwear. With cotton, they furnish useful blends for shirts, nightwear and blouses.

It has been reported by many investigators that alcohol reacts with acrylonitrile in the presence of a strong base. This reaction is being applied to cellulose fibers to give products such as cyanoethylated cottons. The cotton is treated with sodium hydroxide, then with acrylonitrile. This treatment makes the cotton more receptive to dyes and increases the abrasion and stretch resistance. The modified cotton fiber also shows greater retention of strength after exposure to heat and is made permanently by resistant to mildew.<sup>(1)</sup>

The industrial manufacture of acrylonitrile is carried out by several processes as is described below. (1) Ethylene cyanohydrin,<sup>(1)</sup> prepared from ethylene oxide and hydrogen cyanide, is passed over a dehydration catalyst such as alumina or magnesium carbonate. The reaction is carried out at either atmospheric or reduced pressure in the vapor phase at 250-350°C or in the liquid phase.<sup>(2)</sup> (2) In the presence of cuprous chloride and ammonium chloride adjusted to a pH of 1 with hydrochloric acid, hydrogen cyanide has been combined with acetylene to produce the acrylonitrile.<sup>(2-d, 3)</sup>

- 
- (1) J.H. MacGregor and C. Pugh, *J. Chem. Soc.*, 1945, 535; W.P. Utermohlen, Jr., *J. Amer. Chem. Soc.*, 67, 1505 (1945); R.E. Leslie and H.R. Henze, *ibid.*, 71, 3480 (1949); American Cyanamid Co., Brit. Patent, 544,421 (1942).  
 (2) a) H.S. Davis and E.L. Carpenter, Can. Patent, 435,687; *Chem. Abstr.*, 40, 7230 (1946). b) E. L. Carpenter and H. S. Davis, U. S. Patent, 2, 461, 492; *Chem. Abstr.*, 43, 3836 (1949). c) E. L. Carpenter, U. S. Patent, 2, 494, 116; *Chem. Abstr.*, 44, 3006 (1950). d) P. W. Sherwood, *Petroleum Processing*, 1954, 384.  
 (3) a) C. A. Buehler and D. E. Pearson, "Survey of Organic Syntheses," Wiley-Interscience, New York (1970), p.962. b) P. Kurtz, *Ann.*, 572, 28 (1951). c) P. Kurtz, *Petrol. Refin.*, 32 (11), 142 (1953). d) C. W. Bradley and H.S.

(3) In the vapor phase process, when acetylene and hydrogen cyanide are passed over a metallic cyanide catalyst at 400 to 500°C, the main product is acrylonitrile. (4) A most interesting process for manufacturing acrylonitrile from propylene, ammonia, and air has led to successful commercial equipments by Standard Oil Company (Ohio). The catalyst consists, for example, of bismuth phosphomolybdate deposited on silica gel.<sup>(4)</sup> (5) The catalytic oxidation of the allylamine is developed in the laboratories of the Shell Development Co. in Emeryville. It consists in oxidizing allylamine at 450-600°C with air in the presence of steam over silver catalysts, the acrylonitrile being obtained in a yield of about 90%.<sup>(5)</sup> (6) Acetaldehyde and hydrogen cyanide react in the presence of a sodium hydroxide solution to give lactonitrile. The compound thus obtained is treated with water and phosphoric acid at reduced pressure and 600-700°C.<sup>(6)</sup> (7) A mixture of propylene and nitrous oxide is passed over the silver catalyst deposited on silica gel at 450-500°C to obtain acrylonitrile.<sup>(7)</sup> (8) Acrolein is produced from propylene by catalytic

---

Davis, U. S. Patent, 2,385,327; *Chem. Abstr.*, **40**, 1867 (1946). e) E. L. Carpenter and J. S. Mackay, U. S. Patent, 2,688,632; *Chem. Abstr.*, **49**, 8331 (1955). f) E. I. du Pont de Nemours & Co., Brit. Patent, 878,054 (1961); *Chem. Abstr.*, **57**, 7114 (1962). g) L. J. Krebaum, *J. Org. Chem.*, **31**, 4103 (1966).

- (4) a) Standard Oil Co., Belg. Patent, 568,481 (1957), 571,200 (1957), U. S. Patent, 2,904,580 (1959); *Chem. Abstr.*, **54**, 5470 (1960). b) Knapsack-Griesheim A.G., Belg. Patent, 611,239; *Chem. Abstr.*, **57**, 12332 (1962). c) Union Chimique Belge S. A., Brit. Patent, 885,422 (1961); *Chem. Abstr.*, **57**, 5808 (1962).
- (5) a) L. M. Peters, K. E. Marple, T. W. Evans, S.H. McAllister and R. C. Castner, *Ind. Eng. Chem.*, **40**, 2046 (1948). b) H. P. Groll and G. Hearne, *ibid.*, **31**, 1536 (1939). c) Shell Develop. Co., U. S. Patent, 2,375,016 (1945).
- (6) a) A. Wolfram, K. H. Steil and A. Agunte (Knapsack-Griesheim A.G.) U. S. Patent, 2,790,822 (1957); *Chem. Abstr.*, **51**, 14788 (1957). b) K. Sennewald and K. H. Steil, *Chem. Ing. Tech.*, **30**, 440 (1958).
- (7) E.I. du Pont de Nemours & Co., U. S. Patent, 2,736,739 (1956).

gas phase oxidation. Further catalytic reaction with ammonia and oxygen gives the acrylonitrile.<sup>(8)</sup>

The synthesis of the cyano-compounds formed by the direct combination of hydrocarbons and hydrogen cyanide in the silent discharge seems to be interesting and important from both the practical and the theoretical points of view.

Studies concerning the reaction of ethylene alone in electrical discharge have been reported many investigators.<sup>(9)</sup> Moreover, in recent years, the reactions of ethylene and ammonia or oxygen under silent electrical discharge have been investigated by Sugino *et al.*<sup>(10)</sup> and by Tsutsumi *et al.*<sup>(11)</sup> In the previous papers,<sup>(12)</sup> the reactions between hydrocarbon (cyclohexane, ethylene, and propylene) and hydrogen cyanide or hydrogen sulfide in silent discharge were studied. When a mixed gas of ethylene and hydrogen cyanide was discharged in an ozonizer under atmospheric pressure, acrylonitrile could be prepared in one step. Besides this compound, the formation of telomers, such as ethyl, *n*-butyl, and *n*-hexyl cyanides, was also observed. Moreover, when a mixture of ethylene and hydrogen sulfide was discharged in an ozonizer, the main products were ethyl

- 
- (8) a) Distillers Co. Ltd., Brit. Patent, 875,160 (1961); *Chem. Abstr.*, 57, 13628 (1962). b) T. Bewley, U. S. Patent, 2,836,614; *Chem. Abstr.*, 52, 19952 (1958).
- (9) These reports are summarized by C. L. Thomas, G. Egloff and J. C. Morell, *Chem. Revs.*, 28, 1 (1941).
- (10) T. Matsuda, K. Ota 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).
- (11) N. Sonoda, S. Yamamoto, K. Okumura, S. Noda and S. Tsutsumi, "Oxidation of Organic Compounds," Vol. II, *Advances in Chemistry Series 76*, American Chemical Society, Washington (1968), pp. 352-362.
- (12) a) K. Kawamoto, N. Sonoda and S. Tsutsumi, *Bull. Chem. Soc. Japan*, 41, 1376 (1968), b) K. Kawamoto, *ibid.*, 41, 2161 (1968), c) K. Kawamoto and Y. Nishimura, *ibid.*, 42, 1105 (1969). d) Y. Nishimura and K. Kawamoto, *ibid.*, 45, 274 (1972).

mercaptan, *n*-butyl mercaptan, and ethylene dithioglycol. Besides these compounds, the reaction products were confirmed to be diethyl sulfide, *s*-butyl, *n*-hexyl, *n*-propyl, and isopropyl mercaptans, and gaseous products.

The direct synthesis of acrylonitrile from ethylene and cyano-compounds has been established in several patents. (1) Porter and Nesty<sup>(13)</sup> and Sandner and Fierce<sup>(14)</sup> 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. (2) Acrylonitrile was obtained by the addition of cyanogen chloride or cyanogen bromide to ethylene in the presence of aluminum chloride and nitromethane.<sup>(15)</sup> (3) It was found by Oberbacher<sup>(16)</sup> that acrylonitrile could be prepared by the reaction of ethylene with cyanogen at 300-700°C at low pressures.

Francesconi and Giurlo<sup>(17)</sup> reported that when a mixture of ethylene and hydrogen cyanide was subjected to the electrical discharge, ethyl cyanide and ethyl isocyanide were obtained.

In a preceding study,<sup>(12-c)</sup> it was found that the relative amount of acrylonitrile obtained by the reaction between ethylene and hydrogen cyanide in a silent discharge is affected by the substances (Hg(CN)<sub>2</sub>, Cu, CuCN, Al, Zn, and Fe) placed in a glass filter of the special discharge tube.<sup>(18)</sup> It has been reported by many investigators that the formation of ozone

(13) F. Porter and G.A. Nesty, U. S. Patent, 2,445,693; *Chem. Abstr.*, 42, 8209 (1948).

(14) W. J. Sandner and W. L. Fierce, U. S. Patent, 2,803,641; *Chem. Abstr.*, 52, 5449 (1958).

(15) Brit. Patent, 686,692; *Chem. Abstr.*, 48, 8251 (1954).

(16) B. Oberbacher, German Patent, 1,034,625; *Chem. Abstr.*, 54, 11996 (1960).

(17) L. Francesconi and A. Giurlo, *Gazz. Chim. Ital.*, 53, 327 (1923).

(18) M. Suzuki, *J. Electrochem. Soc. Japan*, 24, 207 (1956); T. Naito, "Ozonizer Handbook," Korona Co, Tokyo (1960), pp. 245-258; H. Funahashi, *Yuki*

is affected by the nature of substances of the wall of discharge tube; one side of the discharge tube is replaced with a wall of metallic stuff, such as stainless steel or aluminum. Further, Morinaga and Suzuki<sup>(19)</sup> found that when the ozone formation from oxygen was carried out by using a special type discharge tube with the packing materials (Soda glass,  $2\text{MgO/TiO}_2$ ,  $\text{TiO}_2$ ,  $\text{BaTiO}_3$ , and  $95\text{BaTiO}_3/5\text{SnO}_2$ ), the ozone formation rate increased in a packed discharge tube more than in the same type of ozonizer without packing. However, Lind and Glockler<sup>(20)</sup> found that when ethane was discharged in four different types of discharge tubes, the type of discharge tube did not affect the reaction products greatly. Some secondary differences were found. It has been found by Sahasrabudhey and Deshpande<sup>(21)</sup> that although the influence of the wall catalysts is investigated on hydrogen-carbon monoxide interaction leading to formaldehyde formation, the surface catalysts have little influence on the change.

Frison<sup>(22)</sup> reported that for ozonator electrodes and dielectrics, one of the four arrangements was adapted, in which the discharge took place either between two dielectrics or between a dielectric and a bare electrode. The discharge employed in this experiment was carried out between a dielectric and a bare electrode.

The present study has been undertaken to find how the type of discharge tube influences the reaction between ethylene and hydrogen

---

Gosei Kagaku Kyokai Shi, 11, 262 (1953); F.K. McTaggart, "Plasma Chemistry in Electrical Discharges," Elsevier Publishing Co., Amsterdam/London/New York (1967), pp.35-38.

(19) K. Morinaga and M. Suzuki, *Bull. Chem. Soc. Japan*, 35, 429 (1962).

(20) S. C. Lind and G. Glockler, *J. Amer. Chem. Soc.*, 50, 1767 (1928).

(21) R. H. Sahasrabudhey and S. M. Deshpande, *J. Indian Chem. Soc.*, 28, 377 (1951).

(22) P. Frison, "Ozone Chemistry and Technology," *Advances in Chemistry Series* 21, American Chemical Society, Washington (1959), pp 443-449.

cyanide in a silent discharge, and to establish, if possible, the most optimum conditions for the preparation of acrylonitrile.

### Experimental

*Materials.* The ethylene (research grade) was used without further purification. No impurity was found by gas-chromatographic analysis. (Columns of activated charcoal and dimethylsulfolane were used.) The hydrogen cyanide was prepared according to the procedure of Brauer.<sup>(23)</sup> Purification was carried out by passing the substance over calcium chloride (F) and phosphorus pentoxide (G), as in Fig. 2. The amount of hydrogen cyanide used in each experiment was about a 2 mol.

*Discharge Tubes.* Experiments were carried out by using three different discharge tubes as shown in Fig. 1. (1) The discharge tube (Type

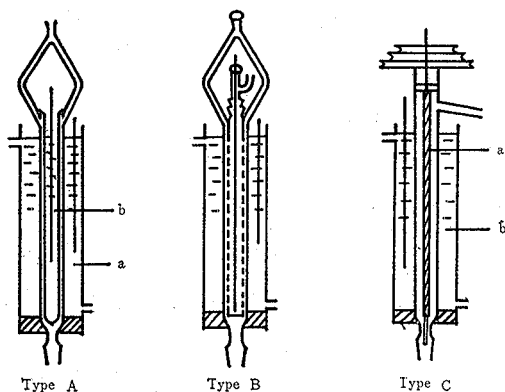


Fig 1. The discharge tubes

A in Fig. 1) used in Experiment No. 1 of Table 1 was a Pyrex tube

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

25 cm in effective length, 3 cm in outside diameter,<sup>(24)</sup> and with a space gap of 0.25 cm. (2) The discharge tube (Type B in Fig.1) employed in Experiment Nos.2 and 3 was similar to that used in the previous paper;<sup>12-c)</sup> this tube was a Pyrex tube with a glass filter 25 cm in effective length and 2 cm in diameter, and with a space gap of 0.25 cm. The packing materials placed in the glass filter were 90 g of copper and 50 g of aluminum, respectively; they were used in the powder state. (3) The discharge tube (Type C in Fig.1) used in Experiment Nos. 4-19 was of the rotational electrode type with a single dielectric as shown in Fig. 1. This tube was a Pyrex tube with a central metal plate electrode(a) which had 25 cm in length, 1.1 cm in width and 0.2 cm thick, and with a space gap of 0.25 cm. The outside (b) of the discharge tube was surrounded by water heated to the operating temperature. Central metal plate electrode was copper, aluminum, nickel, and iron, respectively, and this electrode was rotated at the desired velocity during the period of the discharge reaction.

*Apparatus.* The apparatus illustrated in Fig.2 was used. (1) Ethylene coming from a reservoir (A) was passed over calcium chloride (B), and the ethylene flow was measured by passing it through two calibrated flow meters (C and D). (2) The hydrogen cyanide was prepared in a flask (E) according to Brauer's method.<sup>(23)</sup> (3) The outside (a) of the discharge tube (Type A in Fig.1) was filled with water, and the inner tube (b), with a 3 % copper sulfate solution. (4) Unchanged hydrogen cyanide was absorbed in two bottles (I) (containing a mixture of sodium hydroxide and ferric sulfate). (5) The electrical energy was supplied by a 15-kV transformer (J).

(24) The central glass tube was 2 cm in diameter, and this tube was enclosed in a Pyrex tube 3 cm in outside diameter described above.



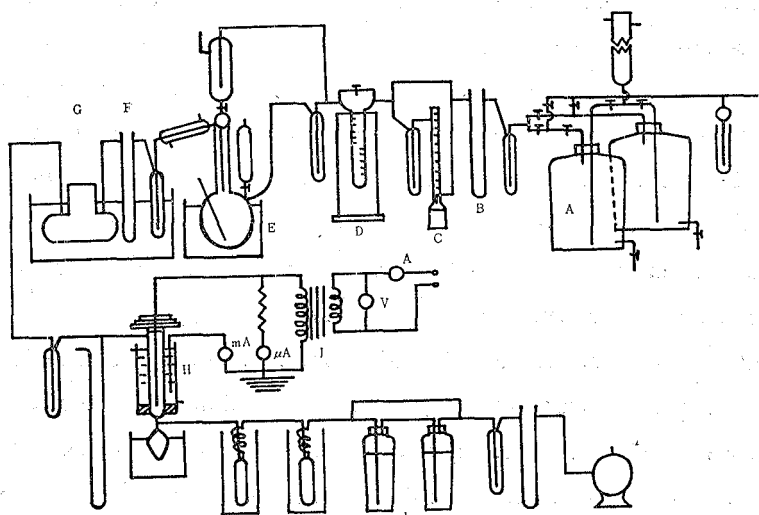


Fig.2 Apparatus

*Procedure.* All the experiments were performed by using a flow system. These discharge tubes were maintained at the operating temperature. A mixture of ethylene and hydrogen cyanide was passed through these discharge tubes at a constant velocity for the period of the reaction. The number of rotation of the central metal plate electrode shown Type C in Fig.1 was performed at 900 and 1380 per min. The number of rotation was determined by using a Toshiba-Stroboscope Apparatus (SS-4B Type). The high tension was applied to the discharge tube from a transformer with a 60-cycle alternating current. The reaction products coming through the discharge tube were separated into a condensable part and non-condensable gases by three ice-cooled traps. The liquid products thus obtained were analyzed by the method described below, while the non-condensable gases were analyzed by gas-chromatography at interval of 30 min.

*Identification and Analysis of the Reaction Product.* The reaction

products were identified by comparing them with the authentic sample<sup>(25)</sup> 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 fraction were identified by observing the formation of the derivatives described below and 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,<sup>(26)</sup> mp 126-128°C, and the picrate of  $\beta$ -piperidinopropionitrile,<sup>(27)</sup> 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. (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.<sup>(28)</sup> The infrared spectrum showed a strong absorption band at 2250 cm<sup>-1</sup>. (3) The other products were identified by comparing their retention times on the gas chromatogram with those of

(25) *s*-Butyl, 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.

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

(27) The picrate of  $\beta$ -piperidinopropionitrile was prepared by Brockway's method; C. E. Brockway, *Anal. Chem.*, 21, 1207 (1949).

(28) H. P. Howells and J. G. Little, *J. Amer. Chem. Soc.*, 54, 2451 (1932).

authentic compounds.

The gaseous products obtained in this experiment were found to be hydrogen, ethane, acetylene, *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 quantitative analysis of the liquid products was performed 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.

### Results and Discussion

When the discharge reactions of hydrogen cyanide with ethylene were carried out under the conditions listed in Table 1, a large number of compounds were obtained in every run. Among these, the identified compounds are summarized in Table 2. The percentage compositions of the reaction products shown in this table are an average of three experiments under constant operating conditions; the fluctuation in the yields of these compounds was less than 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.

The special discharge tubes shown Type B and Type C in Fig.1 were used for the purpose of investigating the effects of the discharge wall on the formation of acrylonitrile. It has been reported by Frison that<sup>(22)</sup> when the discharge reaction is carried out between two dielectrics, for equal discharge density, an applied tension higher than that corresponding to a single dielectric assembly is necessary, and that, therefore,

TABLE 1. INFLUENCES OF THE TYPES OF DISCHARGE TUBE, THE AXIS AND THE NUMBER OF ROTATION, THE MOLAR RATIO OF ETHYLENE TO HYDROGEN CYANIDE, AND THE DISCHARGE TEMPERATURE ON THE YIELD OF ACRYLONITRILE  
(Experimental conditions)

Experiment No.	Type of discharge tube	Rotation Axis	Number	Ethylene used (l)	Velocity (l/hr)	Molar ratio ( $C_2H_4/HCN$ )	Discharge temp. ( $^{\circ}C$ )	Discharge time (hr)	Secondary Voltage (kV)	Current (mA)
1	A <sup>a)</sup>	—	—	40.62	5.08	0.9	30 <sup>e)</sup>	8	15	1.3
2	B-Cu <sup>b)</sup>	—	—	42.49	5.31	1.0	30	8	15	3.0
3	B-Al <sup>c)</sup>	—	—	41.00	5.13	0.9	30	8	15	1.8
4	C <sup>d)</sup>	Cu	1380	38.25	4.78	0.9	30	8	15	3.9
5	C	Al	1380	40.58	5.07	0.9	30	8	15	4.5
6	C	Ni	1380	39.12	4.89	0.9	30	8	15	4.1
7	C	Fe	1380	40.79	5.10	0.9	30	8	15	4.4
8	C	Cu	900	40.64	5.08	0.9	30	8	15	4.0
9	C	Al	900	42.10	5.26	0.9	30	8	15	4.5
10	C	Cu	1380	74.36	9.30	1.7	30	8	15	4.1
11	C	Al	1380	76.33	9.54	1.7	30	8	15	4.4
12	C	Ni	1380	75.27	9.41	1.7	30	8	15	3.9
13	C	Fe	1380	81.27	10.16	1.8	30	8	15	4.3
14	C	Cu	1380	20.23	2.53	0.5	30	8	15	4.5
15	C	Cu	1380	111.64	13.96	2.5	30	8	15	5.3
16	C	Cu	1380	41.31	5.16	0.9	5	8	15	4.2
17	C	Cu	1380	39.72	4.96	0.9	50	8	15	4.3
18	C	Cu	1380	42.18	5.27	0.9	90	8	15	4.5
19	C	Cu	1380	83.89	10.49	1.8	50	8	15	4.5

a) This line shows the result obtained by using the Siemens tube.

b) Type B-Cu was filled with copper powder (90g) as packing material.

c) Type B-Al was filled with aluminum powder (50g).

d) Type C was the discharge tube with the central metal plate electrode which had an effective length of 25 cm, a width of 1.1 cm and a thick of 2 mm.

e) The outside temperature of the discharge tube filled with water was at  $30^{\circ}C$ , and the temperature of the inner tube filled with 3%  $CuSO_4$  solution was at  $30-40^{\circ}C$ .

TABLE 2. INFLUENCES OF THE TYPES OF DISCHARGE TUBE, THE AXIS AND THE NUMBER OF ROTATION, THE MOLAR RATIO OF ETHYLENE TO HYDROGEN CYANIDE, AND THE DISCHARGE TEMPERATURE ON THE YIELD OF ACRYLO-NITRILE (Experimental results).

Experiment No.	Liquid product collected	Reaction product	Conversion efficiency <sup>a)</sup>	Composition of liquid reaction products <sup>b)</sup> (%)							
				Acrylo- nitrile	Ethyl cyanide	<i>n</i> -Butyl cyanide	<i>n</i> -Hexyl cyanide	<i>s</i> -Butyl cyanide	<i>n</i> -Propyl cyanide	Isopropyl cyanide	Unidentified product
	(g)	(g)	(%)								
1	19.68	1.28 <sup>c)</sup>	2.5	47.5	5.6	28.3	T	13.8	2.7	2.1	T
2	21.61	1.01	1.9	73.1	6.6	8.3	0	5.2	3.7	3.1	T
3	18.39	1.08	2.1	54.7	8.1	20.4	0	10.5	3.4	2.9	T
4	21.24	1.16	2.4	66.5	6.6	12.5	0	8.7	3.0	2.7	T
5	16.26	1.14	2.3	63.9	6.3	13.5	0	10.3	3.3	2.7	T
6	17.45	1.06	2.2	64.9	6.3	13.2	0	9.9	3.1	2.6	T
7	19.47	1.05	2.1	66.2	6.5	13.0	0	9.3	2.7	2.3	T
8	14.14	0.97	1.9	66.7	6.3	12.4	0	9.7	2.6	2.3	T
9	17.80	0.95	1.8	64.2	6.6	12.8	0	9.7	3.6	3.1	T
10	4.29	0.88	0.9	41.8	9.2	29.0	0	13.3	3.5	3.2	T
11	2.38	0.67	0.7	38.7	8.1	32.8	0	13.5	3.6	3.3	T
12	1.82	0.34	0.4	39.2	7.5	33.5	0	14.1	3.1	2.6	T
13	0.90	0.26	0.3	43.0	9.2	25.3	0	11.3	5.9	5.3	T
14	27.28	1.07	4.3	75.2	6.0	7.2	0	6.0	3.0	2.6	T
15	0.37	0.32	0.2	13.3	6.2	54.0	0	18.8	4.1	3.6	T
16	18.29	0.61	1.2	86.6	6.2	3.0	0	2.6	0.9	0.7	T
17	19.67	2.18	4.4	53.0	9.8	20.5	0	10.9	3.2	2.6	T
18	16.52	0.94 <sup>d)</sup>	1.8	54.8	7.4	19.6	0	9.8	4.4	4.0	T
19	1.18	0.42	0.4	27.1	7.6	42.1	0	15.5	4.1	3.6	T

T : Trace

a) The conversion efficiency was given by (grams of reaction product per grams of ethylene used)×100.

b) The yields of each compound produced were given by (grams of each compound per grams of total reaction product)×100.

c) In this case, the traces of *n*-amyl and isoamyl cyanides were obtained.

d) A solid brown deposit was formed on the discharge wall.

the energy of the discharge with two dielectrics can only be less than that of the single dielectric assembly. Thus, the discharge reaction used in this experiment was carried out between a dielectric and a bare electrode. Derived from the Siemens Ozonator, the discharge method used in Experiment Nos. 4-19 of Table 1 differs only in the ingenious method of centering the high tension electrode. A vertical glass dielectric is surrounded by water, which serves as the electrode. The high tension electrode is spaced concentrically within the glass tube, leaving an annular discharge space.

*Influence of the Discharge Wall on the Acrylonitrile Formation.* As may be seen from Experiment Nos. 1, 2, and 4 in Table 2, there are the differences among these discharge tubes: It has been found that when the Siemens tube is used, the yields of the reaction product and *n*-butyl cyanide formed by the telomerization between ethylene and hydrogen cyanide increase, and that when one side of discharge tube is replaced by the walls of the glass filter filled with copper and aluminum powders or of the central metal plates as shown Type C in Fig. 1, the yields of the reaction products decrease slightly, while the proportion of acrylonitrile in the liquid products increases. When the special discharge tubes were used, the component of the gaseous products was similar to that of the gaseous products obtained in using the Siemens tube. The liquid product pattern was somewhat simplified by changing glass wall to metal wall. For example, the gas chromatogram showed sixteen peaks for the products from Experiment No. 1 (using the glass wall), but only ten peaks for Experiment Nos. 2-19 (using the metal wall). Therefore, the selectivity was a little higher in the presence of metal wall than in its absence (glass wall). As may be seen from Experiment Nos. 2 and 3 in Table 2, the yield of the reaction products and the proportion of acry-

lonitrile in the liquid products are affected by the packing materials; when the discharge wall of the glass filter is filled with copper powder, the high yield of acrylonitrile is obtained.

Comparing a wall of the glass filter filled with copper powder (Experiment No.2) with a wall of the central copper plate (Experiment No.4), it has been found that when the wall of the glass filter is used, the yield of the reaction product and the proportion of *n*-butyl cyanide in the liquid product decrease, while the proportion of acrylonitrile increases. As may be seen from Experiment Nos. 4, 5, 6, 7, 10, 11, 12, and 13 in Table 2, the yield of the reaction products varied slightly with the central metal plates used as the discharge wall. When the copper plate was used, the yield of the reaction product was at its maximum. The yield of the reaction products obtained with various metal plates is in the following order: Cu > Al > Ni > Fe. In order to extend the residence time in the discharge tube of reactants, the number of rotation of central plate was changed. As may be seen from Experiment Nos. 4, 5, 8, and 9 in Table 2, the yield of the reaction products depends upon the number of rotation of the central metal plate electrode; it has been found that increasing the number of rotation increases the yields of the liquid product and the gaseous product.

*Influence of the Molar Ratio of Ethylene to Hydrogen Cyanide on the Acrylonitrile Formation.* In order to check the molar ratio effects on the discharge reaction between ethylene and hydrogen cyanide, the reaction was carried out with various ratios of ethylene to hydrogen cyanide concentration as shown in Experiment Nos. 4, 10, 14, and 15 of Table 1. As may be seen from the results of these experiments shown in Table 2, the yield of the reaction products depends upon the molar ratio

of ethylene to hydrogen cyanide; it has been found that when the molar ratios of ethylene to hydrogen cyanide are in the region of 0.5:1 to 0.9:1, the maximum yield of the reaction products is obtained. Furthermore, the distribution of the products depends upon the molar ratios of reactants as follows: (1) The proportion of acrylonitrile in the liquid products increases at high ratios of hydrogen cyanide to ethylene (2) On the other hand, *n*-butyl cyanide and *s*-butyl cyanide decrease with the increase in the ratio of hydrogen cyanide to ethylene. Thus, it may be said that the yield of telomer with  $n=2$  (*n*-butyl cyanide) is favored by a low ratio of the hydrogen cyanide to the ethylene concentration. In the case of the special discharge tubes, the formation of *n*-hexyl cyanide and one-to-four or more products could not be observed by gas-chromatographic analysis.

*Influence of the Discharge Temperatures on the Acrylonitrile Formation.* To find the difference in the yield of the reaction products on varying the discharge temperature and the optimum temperature for the formation of acrylonitrile, the discharge reaction was performed at 5, 30, 50, and 90°C as shown in Experiment Nos. 4, 16, 17, and 18 of Table 1. As may be seen from the results of these experiments shown in Table 2, the conversion efficiency [(grams of reaction product/grams of ethylene used)  $\times 100$ ] depends upon the temperature at which the discharge is carried out; it has been found that when the discharge reaction is performed at 90°C, a solid brown deposit is formed on the discharge wall, while the yield of solid product thus obtained increases with a rise in the discharge temperature, that when the discharge reaction is performed over the range of discharge temperatures from 5 to 50°C, the yields of the liquid products and the gaseous products increase with a rise in the discharge temperature, and that in the case of a



high-temperature discharge, the proportion of acrylonitrile in the liquid products decreases, while the yields of *n*-butyl cyanide and *s*-butyl cyanide increase. This fact indicates that the telomerization of this sort is much affected by the discharge temperature. A low temperature favors the formation of acrylonitrile.

*The Mechanism of the Formation of the Main Products Obtained by the Reaction of Ethylene and Hydrogen Cyanide.* It was reported by Egloff *et al*<sup>(9)</sup> that the radical from ethylene in the electrical discharge was a vinyl radical, and that it was produced by breaking a carbon-hydrogen bond. Tsutsumi<sup>(29)</sup> reported that the vinyl radical was obtained by two molecular processes.

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.

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

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

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 represented as follows: Ethyl cyanide may be formed by three paths (1) the addition of the cyano radical to ethylene, and then the reaction of the hydrogen cyanide with the  $\dot{\text{C}}\text{H}_2\text{-CH}_2\text{-CN}$  radical so formed, (2) the combination of the ethyl radical (obtained by two molecular processes) and the cyano radical, (3) the formation of acrylonitrile by the combination of the vinyl radical and the cyano radical, and then the addition of hydrogen atoms to the compound thus obtained. *n*-Butyl cyanide may be formed by the addition of the  $\dot{\text{C}}\text{H}_2\text{-CH}_2\text{-CN}$  radical to ethylene, and then the reaction of a hydrogen cyanide with  $\dot{\text{C}}\text{H}_2(\text{CH}_2)_3\text{CN}$  radical so formed. The addition reaction of the  $\text{C}_6\text{H}_{12}\text{CN}$  radical to ethylene in these reaction mechanisms need not be considered, since no products beyond *n*-hexyl cyanide were obtained.

Beer and Besprozvanniy<sup>(30)</sup> found, from their data on the telomerization of ethylene in carbon tetrachloride and chloroform, that compounds 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  $\text{CH}_2$  and the electrophilic  $\text{CCl}_3$  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*-he-

(30) A. A. Beer and M. A. Besprozvanniy, *Khim Naukai Prom.*, 4, 547 (1959).

xyl 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.

*s*-Butyl cyanide may be formed by two paths; (1) the reaction between hydrogen cyanide or ethylene and acrylonitrile, the addition of  $\text{CH}_3\text{-}\dot{\text{C}}\text{HCN}$  radical thus obtained to ethylene and then the reaction of the  $\text{CH}_3\text{-CHCN-CH}_2\text{-}\dot{\text{C}}\text{H}_2$  radical and hydrogen cyanide,<sup>(31)</sup> and (2) the isomerization of *n*-butyl cyanide.<sup>(32)</sup>

### Summary

The present investigation has been undertaken in order to find the difference in the reaction products on varying the discharge wall and the most suitable conditions for the preparation of acrylonitrile. The discharge reaction between ethylene and hydrogen cyanide was carried out by using three kinds of discharge tubes. When one side of the discharge tube was replaced by four different metal plates, *i. e.* copper, aluminum, nickel, and iron, the yield of the reaction products varied slightly with the sort of the metal plates. The maximum yield of the reaction product was obtained by using copper plate as discharge wall. The proportion of acrylonitrile in the liquid products increased, when the molar ratios of ethylene to hydrogen cyanide were in the region of the ratios from 0.5:1 to 0.9 : 1. Furthermore, a low temperature for

(31) The present authors have found that when the reaction between acrylonitrile and ethylene in a silent discharge is carried out, the main product is *s*-butyl cyanide, and that besides this compound, the reaction products consist of ethyl, *n*-butyl, 2-hexyl, *n*-propyl and isopropyl cyanides, and gaseous products.

(32) It has been found by the present authors that when the reaction of *n*-butyl cyanide and ethylene in a silent discharge is performed, a small amount of *s*-butyl cyanide is obtained.

discharge favored the formation of acrylonitrile. The yield of the telomer with  $n=2$  (*n*-butyl cyanide) increased with an increase in a molar ratio of ethylene to hydrogen cyanide, and with a rise in the discharge temperature.