By-products of Acrylonitrile Synthesis from Acetylene and Hydrocyanic Acid. I. Neutral Constituents

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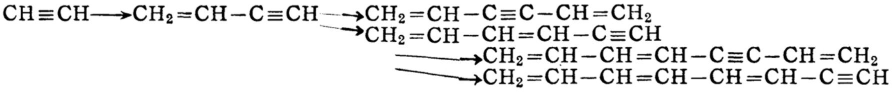
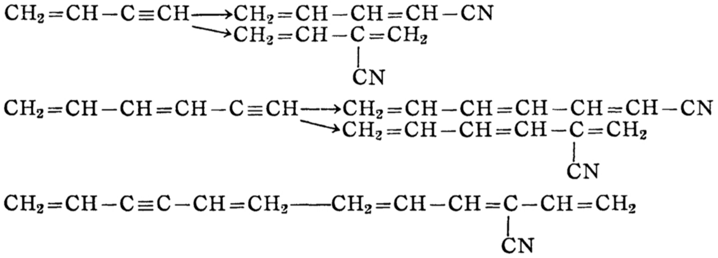
For several years the present author has been studing the vapor phase synthesis of acrylonitrile from acetylene and hydrocyanic acid. It is very likely that many reaction products are produced in this process because the starting materials are very reactive. It seems to be very important from the scientific as well as from the industrial standpoint to detect the byproducts which are produced by this process.

No report seems to have been made on this detection, although some reports have been made on that in the liquid phase synthesis using the so-called Nieuwland's catalyst[1]. According to these reports, what was considered to be a reaction products of acetylene and hydrocyanic acid was only cyanobutadiene: no separation has been carried out between 1- and 2-cyanobutadiene. No report has been made on the formation of higher nitriles. The following substances have been known as the polymerization products of acetylene alone using Nieuwland's catalyst: (Nieuwland[2], Georgieff[3].



$$\begin{aligned}\mathrm{CH{\equiv}CH} &\longrightarrow \mathrm{CH_2{=}CH{-}C{\equiv}CH} \longrightarrow \mathrm{CH_2{=}CH{-}C{\equiv}C{-}CH{=}CH_2}\\ &\phantom{\longrightarrow \mathrm{CH_2{=}CH{-}C{\equiv}CH}} \longrightarrow \mathrm{CH_2{=}CH{-}CH{=}CH{-}C{\equiv}CH}\\ &\phantom{\longrightarrow \mathrm{CH_2{=}CH{-}C{\equiv}CH}} \longrightarrow \mathrm{CH_2{=}CH{-}CH{=}CH{-}C{\equiv}C{-}CH{=}CH_2}\\ &\phantom{\longrightarrow \mathrm{CH_2{=}CH{-}C{\equiv}CH}} \longrightarrow \mathrm{CH_2{=}CH{-}CH{=}CH{-}CH{=}CH{-}C{\equiv}CH}\end{aligned}$$

In the case of the reaction between acetylene and hydrocyanic acid, formation of olefinic nitriles is considered possible because hydrocyanic acid may be added to the above mentioned polymerization products of acetylene as follows:



$$\begin{aligned}\mathrm{CH_2{=}CH{-}C{\equiv}CH} &\longrightarrow \mathrm{CH_2{=}CH{-}CH{=}CH{-}CN}\\ &\longrightarrow \mathrm{CH_2{=}CH{-}}\underset{\mathrm{CN}}{\underset{|}{\mathrm{C}}}\mathrm{{=}CH_2}\\ \mathrm{CH_2{=}CH{-}CH{=}CH{-}C{\equiv}CH} &\longrightarrow \mathrm{CH_2{=}CH{-}CH{=}CH{-}CH{=}CH{-}CN}\\ &\longrightarrow \mathrm{CH_2{=}CH{-}CH{=}CH{-}}\underset{\mathrm{CN}}{\underset{|}{\mathrm{C}}}\mathrm{{=}CH_2}\\ \mathrm{CH_2{=}CH{-}C{\equiv}C{-}CH{=}CH_2} &\relbar\joinrel\relbar \mathrm{CH_2{=}CH{-}CH{=}}\underset{\mathrm{CN}}{\underset{|}{\mathrm{C}}}\mathrm{{-}CH{=}CH_2}\end{aligned}$$

Results and Discussion

A. Reaction Conditions and By-products.—A carrier, reaction temperature, and composition of the feed gas mixture are factors responsible for kinds and amounts of the by-products in the acrylonitrile synthesis from acetylene and hydrocyanic acid using zinc oxide as catalyst.

The author's studies have revealed that the use of some kinds of carrier seems to result in the formation of acetonitrile and basic by-products in a greater amount.

In the present experiment, pumice stone has been used as carrier and the reaction has been carried out at around 400°C[4].

TABLE I

BOILING POINTS AND INFRARED SPECTRA OF CONSTANT BOILING FRACTIONS

Fraction No.	Boiling point °C/mmHg	Distillate cc.	Infrared absorption spectra (μ) C≡N a*	b*	C=C c*	⌬ d*	CH$_2$ e*	C=O f*	OH g*	**
A-2	95.8–97.0	6.5								(1)
A-4	121.5–120	5.5	++	+	++	±	+	−	+	(2)
B-4	73–75/75	12.5	++	+	++	+	+	−	±	(3)
D-3	80–82/33	5.0	+		+	±	+	+	−	
D-5	85–86/33	4.7	+		+	±	+	++	+	
D-10	93/33	3.3	++		+	+	+	+	−	(4)
E-3	69/7									(5)

* Wave length (μ) a, 4.48–4.51 (conj.); b, 4.44 (nonconj.); c, 6.07–6.11; d, 6.68–6.70, 6.21–6.25; e, 3.4; 6.8; f, 5.8; g, 2.83–2.89.

** The substances which may be expected to exist in the above mentioned fractions are listed below with their literature values of boiling points °C/mmHg.

(1) Propionitrile (identified).

(2) 2-Cyanobutadiene, 24–31/30, 30–40/40; *n*-octane 124.

(3) *p*-Xylene 136; *m*-xylene 139; *o*-xylene 141; ethylbenzene 136; styrene 146; 1-cyanobutadiene 140, 135–8.

(4) Benzonitrile (identified) 190.6, 103.9/50; 1-cyanohexatrine, 56–57/2–3.

(5) Naphthalene (identified).

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[1] A. Cambron, P.B. 19678; B.L. Hasche and J.G. McNally, P.B. 34813; P.B. 81283; P.B. 47715.

[2] J.A. Nieuwland, W.S. Calcott, F.B. Downing and A.C. Carter, *J. Am. Chem. Soc.*, **53**, 4197 (1931); J.A. Nieuwland, U.S. Patent, 1811, 959 (1931).

[3] K.K. Georgieff, W.J. Cave and K.G. Blaikie, *J. Am. Chem. Soc.*, **76**, 5494 (1954).

[4] Considerable variation of temperature by local heating in the reaction tube was observed.

B. Separation of Neutral Substances.—The intermediate distillation fraction between the two main reaction-products, acrylonitrile and succinodinitrile, was divided into three parts, i. e., neutral, basic and acidic.

The neutral part was fractionally distilled through a Stedmantype column (plate number, 20). And the constant boiling fractions were obtained, i. e., A–2(liq.), A–4(liq.), B–4 (liq.), D–3(liq.), D–5(liq.), D–10(liq.), E–3(sol.) (Table I).

A–2 was treated with thioglycolic acid and hydrogen chloride, resulting in the formation of crystals which melted at 123–124°C (decomp.). The melting point corresponded with that of α-iminopropylmercaptoacetic acid hydrochloride $CH_3 \cdot CH_2 \cdot C(SCH_2COOH) : NH \cdot HCl$ in literature[5].

D–10 was hydrolyzed by a 75% sulfuric acid solution to form benzoic acid with a yield of 50–70%. So it was confirmed that D–10 contained benzonitrile in the above mentioned ratio.

E–3 solidified to crystals melting at 80°C and was identified to be naphthalene by a mixed melting test.

The principal infrared absorption bands of A–4, B–4, D–3, D–5, and D–10 are also shown in Table I.

The most marked and common to all samples has been found to be the characteristic absorption of the nitrile radical (ν–C≡N). The absorption bands are observed at two kinds of wave length, 4.44 μ and 4.48–4.51 μ. According to Kitson et al.[6] nitriles nonconjugated with an olefinic bond give an absorption band at $4.44 \pm 0.02\,\mu$; nitriles conjugated with an olefinic bond give an absorption band at $4.49 \pm 0.02\,\mu$. Each sample indicates a marked absorption of the conjugated nitrile, but A–4 and B–4 are accompanied by a weak nonconjugated nitrile absorption.

Another common absorption observed is that of the olefinic bond. The absorption bands are observed at 3.24–3.29 μ (ν C–H), 6.07–6.11 μ (ν–C=C–).

D–10 demonstrates the absorption of the benzene nucleus more markedly than that of the olefinic bond.

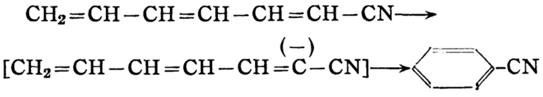
The absorption bands of the acetylenic bond at 3.0 μ (ν≡C–H) and 4.71–4.78 μ (ν–C≡C–) are absent. (Acetylenic compounds seem to have disappeared in these samples during purification, especially during fractional distillation.)

Qualitatively the absorption of D–10 may be regarded as a superposition of absorption of both benzonitrile and 1-cyanohexatriene.

The above mentioned results suggest the existence of 2-cyanobutadiene (cyanoprene) in A–4, 1-cyanobutadiene in B–4, 3-cyanohexatriene in D–3, 2-cyanohexatriene in D–5, and 1–cyanohexatriene besides benzonitrile in D–10.

There also exist absorption bands at 3.4 μ, and 6.8 μ which are considered to be absorption of the methyl or methylene radical. This fact may be explained, considering the existence of nitriles obtained through partial reduction of the above-mentioned unsaturated nitriles, since the existence of propionitrile has been confirmed. Weak absorption of benzene nucleus is somewhat observed in fractions other than D–10. This may be due to the presence of substances having nothing to do with the nitriles.

Formation of benzonitrile seems due to a ring formation of cyanohexatrienes, and especially 1-cyanohexatriene seems easily to aromatize at higher temperature.



$$CH_2=CH-CH=CH-CH=CH-CN \longrightarrow$$
$$[CH_2=CH-CH=CH-CH=\overset{(-)}{C}-CN] \longrightarrow$$

Other experimental results supporting these suggestions will be reported in following papers.

Experimental

(A) Reaction of Acetylene and Hydrocyanic Acid.—*1) Reaction Tube.*—A stainless steel tube with inner diameter of 6 cm., length of heated part 100 cm. (heated directly without bath), length of part packed with catalyst 60 cm.

2) Catalyst.—A carrier of pumicestone of 8–10 mm. diameter was surmounted with zinc hydroxyde (precipitated) which was burnt in the reaction tube at the reaction temperature to form zinc oxide.

3) Reaction Conditions and Results.—These are shown in Table II.

(B) Chemical Separation of the Intermediate Fraction.—The above-mentioned intermediate fraction (242.5 g.) was dissolved in the same amount of ether and treated with a 25% aq. sodium hydroxide solution and then with a 2% aq. hydrochloric acid solution, resulting in the separation of 5 g. (containing water) of the acidic part, 15 g. (containing water) of the basic part, and 229 g. (containing water) of the neutral part.

(C) Fractional Distillation of the Neutral Part.—The neutral part (liquid, 229 g.) was roughly fractionated into A, B, C, D and E by distillation using a Claeisen-flask under reduced pressure. By further fractionating the respective fractions using a Stedman-Type distillation column (with a brass net, plate number 20) under proper pressure, the results shown in Fig. 1–4 were obtained.

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[5] F.E. Condo, E.T. Hinkel, A. Fassero and R.L. Shriner, *J. Am. Chem. Soc.*, 59, 230 (1937).

[6] R.E. Kitson and N.E. Griffith, *Anal. Chem.*, 24, 334 (1952).

TABLE II

REACTION OF ACETYLENE AND HYDROCYANIC ACID

Expt. No.	Heating temp. °C	Temp. in reaction tube °C	reaction time hrs.	C_2H_2 /HCN	Charg. HCN g.	Consum. HCN g.	Acrylonitrile g.	Intermediate fraction g.	Succinodinitrile g.
1	300–340	330–480	36.5	3.3	716	447	495	30	50
2	300–360	370–510	32	3.2	637	396	376	28.5	53
3	310–390	370–560	32	4.4	529	220	306	103	47
4	350–380	380–560	32	3.9	561	255	294	81	50

Total amounts:
(a) Acrylonitrile 1471 g.
(b) Intermediate fraction 242.5 g.
(c) Succinodinitrile 160 g.

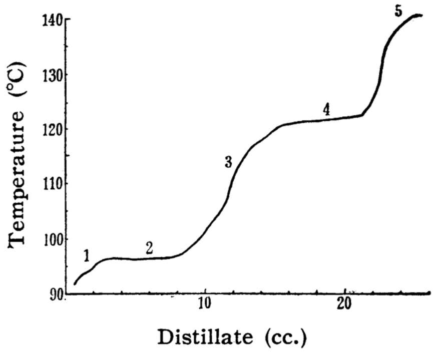

Fig. 1. Distillation curve of fraction A (atm. press.).

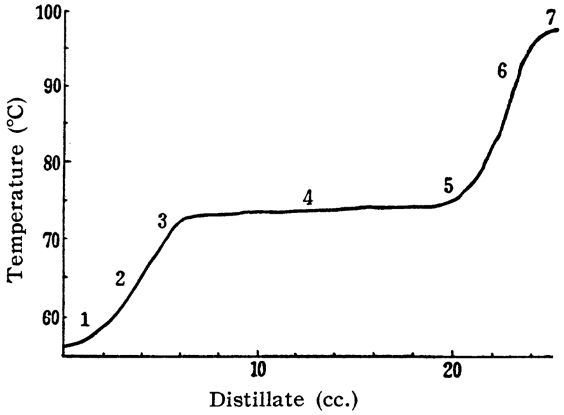

Fig. 2. Distillation curve of fraction B, C (75 mmHg).

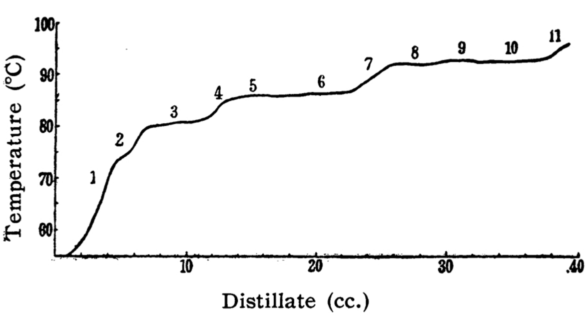

Fig. 3. Distillation curve of fraction D (33 mmHg).

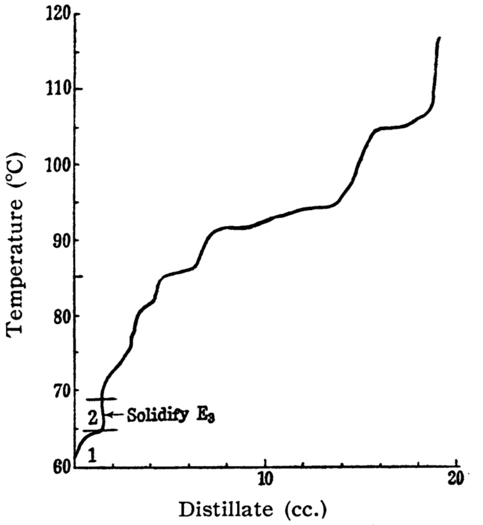

Fig. 4. Distillation curve of fraction E (7 mmHg).

(D) Preparations of Crystalline Derivatives. —*1*) *Propionitrile.*—A-2 fraction (1 g.) and thioglycolic acid (2 g.) were dissolved in dry ether and tnen treated with dry hydrogen chloride gas under cooling with ice from outside. It was then allowed to stand in a refrigerator for half an hour to form white crystals. It was filtered and dried in a desiccator to form 0.5 g. of crystals melting at 123–124°C (decomp.). The melting point (decomposition) of α-iminopropylmercatoacetic acid hydrochloride so far reported is 124°C.

2) *Benzonitrile.*—The mixture of D-10 fraction (1.0 g.) and a 75% aq. sulfuric acid solution (5 cc.) together with sodium chloride (0.2 g.) was heated at 160°C and then at 190°C for half an hour. each. After cooling the reaction product was added to 20 g. of ice. The precipitate was filtered. It was dissolved in aq. potassium carbonate solution and the insoluble substances were filtered off. One gram of black insoluble solid was obtained after drying in a disiccator. The filtrate was made acidic with sulfuric acid and then allowed to stand over night. The precipitate was filtered and dried in a desiccator to form 0.85 g. of crystals which melted at 121–121.5°C. The crystals were recrystallized from 20 cc. of water. It was dried in a desiccator to form 0.65 g.

of crystals which melted at 121–121.5°C. These crystals mixed with benzoic acid melted at 121.2–121.7°C, showing no melting point depression.

Anal. Found: C. 68.69; H, 4.97. Calcd. for $C_7H_6O_2$: C, 68.84; H, 4.95%.

3) *Naphthalene.*—A solid separated in E-3 fraction melted at 80.2°C. It melted at 81.8°C after recrystallization from methanol. It melted at 81.8°C when mixed with naphthalene showing no melting point depression.

Anal. Found: C, 93.63; H, 6.28. Calcd for $C_{10}H_8$: C, 93.71; H, 6.29%.

(E) Infrared Absorption Spectra.—Fig. 5–9 show infrared absorption spectra of A-4, B-4, D-3, D-5, D-10 fractions (Perkin Elmer C12).

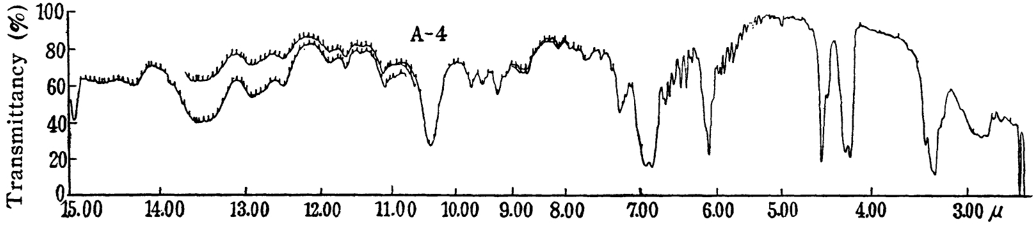

Fig. 5. Infrared absorption spectra of A-4.

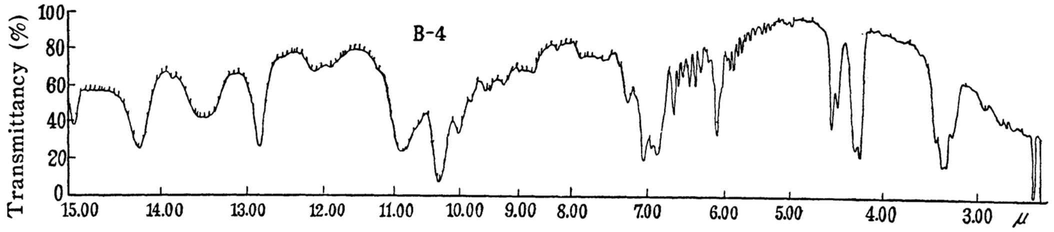

Fig. 6. Infrared absorption spectra of B-4.

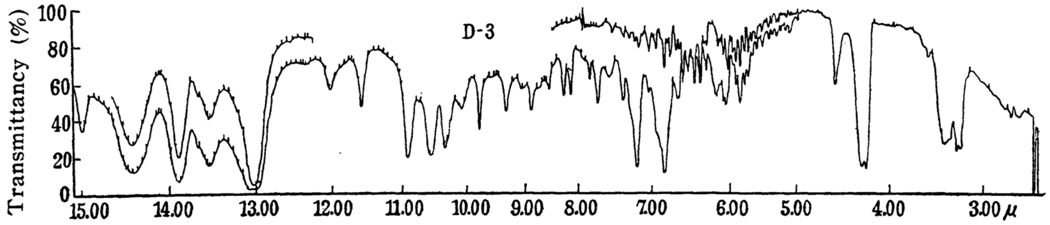

Fig. 7. Infrared absorption spectra of D-3.

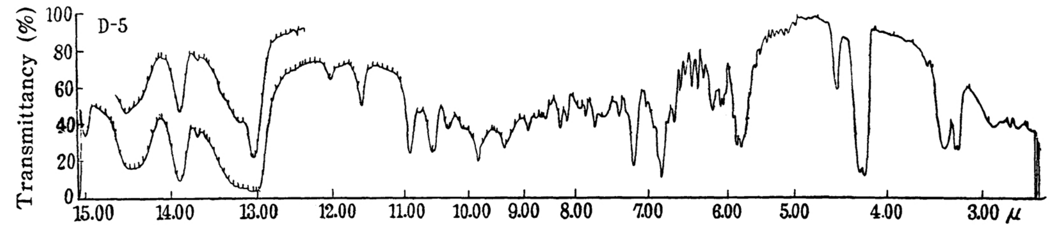

Fig. 8. Infrared absorption spectra of D-5.

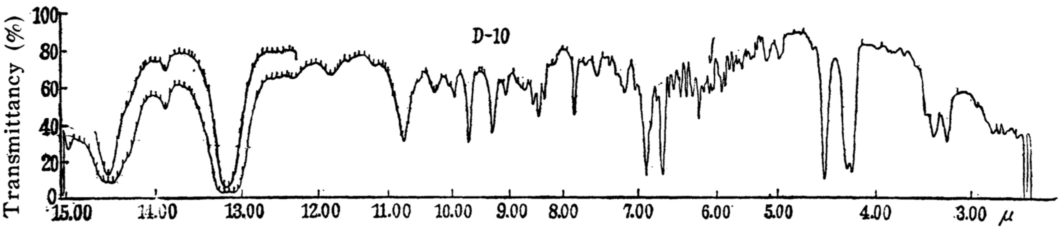

Fig. 9. Infrared absorption spectra of D-10

Summary

By distilling the reaction products of the vapor phase acrylonitrile synthesis from acetylene and hydrocyanic acid an intermediate fraction was obtained between two main fractions, acrylonitrile and succinodinitrile. The neutral portion of the intermediate fraction was carefully distilled through an efficient column and separated into constant boiling fractions. From these fractions propionitrile, benzonitrile naphthalene were isolated and identified as the byproducts. On the basis of the boiling points and the infrared spectra of other fractions, the presence of unsaturated nitriles such as 1-cyanobutadiene, 2-cyanobutadiene, 1-cyanohexatriene, 2-cyanohexatriene, 3-cyanohexatriene as the constituents of the neutral portion was suggested.

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