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The Dechloro-addition of β-Chloropropionitrile to Acrylonitrile with a Sodium Amalgam

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The reaction of a mixture of β-chloropropionitrile, acrylonitrile, and water with a sodium amalgam was investigated. The main product was adiponitrile, which was formed mainly *via* a route consisting of three steps: I. The replacement of the chloride of β-chloropropionitrile with sodium. II. The addition of the organometallic intermediate formed to acrylonitrile. III. The replacement of the sodium in the final intermediate with hydrogen. The amount formed through the Wurtz reaction was small. The by-products were propionitrile, acrylonitrile, polymers of acrylonitrile, and organometallic compounds. The details of this reaction are given in this paper.

Adiponitrile has attracted much attention from industry in connection with the production of hexamethylenediamine, the raw material of Nylon-6,6, which has been usually synthesized from adipic acid or butadiene. Recently the dimerization of acrylonitrile has aroused interest because of its simplicity.

The methods of dimerization may mainly be classified into two from the industrial point of view: The method using the various kinds of alkali metal amalgams, and the electrolytic method using an aqueous or nonaqueous solvent containing McKee's salt as a supporting salt. By the former method, adiponitrile was, in 1949, obtained by the use of a sodium amalgam, but in a yield of only 5%.[1] The yield was increased to 62% (based on the acrylonitrile) by the use of a potassium amalgam and 20 wt% hydrochloric acid, but the efficiency of the amalgam consumed was only 12%.[2] In a similar reaction, adiponitrile was formed in a 75% yield with an alkali metal amalgam in an acidic medium in the presence of a catalyzer, such as phenol, hydroquinone, or aromatic amines, and a promotor, such as ferrous, ferric, nickel, or cobalt ions, and with the addition of acetone.[3] However,

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[1] O. Bayer, *Angew. Chem.*, **61**, 238 (1949).

[2] I. L. Knunyants and N. S. Vyazankin, *Izvest. Akad. Nauk SSSR, Otdel Khim. Nauk*, **1957**, 238.

[3] A. Katchalsky, D. Vofsi and J. I. Padova, Israeli Pat. 13842, 13844 (1961).

many polymers of acrylonitrile were produced in this case.

The latter method has been reported on by Baizer since 1964;[4] much acrylonitrile was dissolved into an aqueous solution containing a high concentration of McKee's salt (for instance, tetraethylammonium *p*-toluenesulfonate), and then the solution was electrolytically dimerized. The yield reached almost 100%, and no by-products were formed. This method appears industrially promising.

The hydrodimerization of acrylonitrile has been investigated in our laboratory for the last several years, using an alkali metal amalgam in an acidic medium, in order to clarify the mechanism and the various factors of the reaction.[5]

We have found that the efficiency of the amalgam consumed was only 32% at most; the rest of the amalgam consumed was wasted in the formation of hydrogen gas. These reactions were, however, carried out in an aqueous medium. Therefore, the reaction in a non-aqueous medium was examined, but here a greater quantity of polymers of acrylonitrile was produced. The lack of a proton donor, such as water or alcohol, in the reaction system gave many organomercuric compounds.

In 1963, Knapsack proposed a method of producing adiponitrile[6] in which a mixture of β-chloropropionitrile, acrylonitrile and a small quantity of water was treated with alkali metal amalgam. The mechanism suggested was as follows:

$$1.\ \mathrm{XCH_2CH_2CN + M\text{-}Hg} \rightarrow \dot{\mathrm{C}}\mathrm{H_2CH_2CN + MX + Hg}$$

$$2.\ \dot{\mathrm{C}}\mathrm{H_2CH_2CN + CH_2{=}CHCN} \rightarrow \mathrm{NCCH_2CH_2CH_2}\dot{\mathrm{C}}\mathrm{HCN}$$

$$3.\ \dot{\mathrm{C}}\mathrm{H_2CH_2CN} \rightarrow \mathrm{CH_2{=}CHCN} + \dot{\mathrm{H}}$$

$$4.\ \mathrm{NCCH_2CH_2CH_2}\dot{\mathrm{C}}\mathrm{HCN} + \dot{\mathrm{H}} \rightarrow \mathrm{NC(CH_2)_4CN}$$

$$5.\ \dot{\mathrm{C}}\mathrm{H_2CH_2CN} + \dot{\mathrm{H}} \rightarrow \mathrm{CH_3CH_2CN}$$

$$6.\ 2\ \dot{\mathrm{C}}\mathrm{H_2CH_2CN} \rightarrow \mathrm{NC(CH_2)_4CN}$$

$$7.\ 2\ \dot{\mathrm{C}}\mathrm{H_2CH_2CN} \rightarrow \mathrm{CH_3CH_2CN + CH_2{=}CHCN}$$

We have now developed a method similar to that of the Knapsack method in the course of our investigation of how to raise the efficiency of the alkali metal in the amalgam method. The factors affecting the reaction were not known, and the mechanism proposed by Knapsack was very doubtful; we undertook our investigation in order to clarify these problems.

Experimental

Acrylonitrile, Ethyl Acrylate and Methyl Acrylate. Commercial reagents were used after drying over "Drierite" and after distillation. The acrylates were distilled under a nitrogen atmosphere, and the distillates were kept under refrigeration in a brown bottle. Bp 78—79°C, 80—84°C, and 100—101°C respectively.

β-Chloropropionitrile, Ethyl β-Chloropropionate, and Methyl β-Chloropropionate. β-Chloropropionitrile was prepared as in the literature.[7] Bp 73—74°C/30 mmHg.

Ethyl β-chloropropionate and methyl β-chloropropionate were prepared by methods similar to the one described in the literature.[7] Ethyl β-chloropropionate: yield 80%, bp 161°C/760 mmHg; methyl β-chloropropionate: yield 72.5%, bp 147—148°C/760 mmHg.

Hydroquinone. Commercial hydroquinone was used without further purification.

Sodium Amalgam. The sodium amalgam was prepared by the electrolysis of a sodium hydroxide solution, using nickel as a cathode. The concentration of the amalgam was measured by titration.

Apparatus and an Example of the Reaction Procedure. β-Chloropropionitrile (0.3 mol), acrylonitrile (0.2 mol), and water (0.5 wt% of reaction mixture) were poured in a 100 m*l*, four-necked, round-bottomed flask equipped with a condenser, a thermometer, a dropping funnel, and a stirrer. The sodium amalgam (sodium 0.5 wt%, 0.1 g atom) was dropped from the funnel into the mixture with vigorous stirring. The temperature was kept between 40 and 42°C with water cooling. After 80 min, the reaction mixture was poured into a separatory funnel, and the amalgam separated was introduced into 4 N hydrochloric acid. The amount of residual sodium was determined quantitatively by the back titration of the acid. The pure water was charged into the separatory funnel to dissolve the neutral salt formed. Then the organic layer was separated from the aqueous layer and the aqueous layer was extracted with chloroform several times. All the organic parts were collected together and then analyzed by vapor-phase chromatography. The acrylonitrile and propionitrile were measured on a four-meter column packed with 10% dioctyl sebacate on diasolid M at 120°C. The β-chloropropionitrile was analyzed on a two-meter column packed with 10% silicone oil D. C. 550 on diasolid M at 120°C. The adiponitrile was analyzed on a three-meter column containing 10% diethyleneglycol sebacate on diasolid M at 200°C. The polymers of the yellow solid formed were not examined.

The deuterated compounds were analyzed with a mass spectrometer (Hitachi RMU-6E), using the ionization temperature of 110°C. The deuteration was determined by measuring the heights of the parent peak (P) and the (P−1) peak; the adiponitrile and the deuterated adiponitrile were decomposed independently, and

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[4] M. M. Baizer, a) *Tetrahedron Letters*, **15**, 973 (1961); b) *J. Electrochem. Soc.*, **111**, 215 (1964); c) *J. Org. Chem.*, **29**, 1670 (1964).

[5] T. Osa, A. Misono, these results are under contribution to "*Kyogyo Kagaku Zasshi (J. Chem. Soc. Japan, Ind. Chem. Sect.)*."

[6] K. Senneward, A. Ohorodnik, H. Gudernatsch and H. Vierling, German Pat. 1151791 (1963).

[7] R. Stewart and R. H. Clark, *J. Am. Chem. Soc.*, **69**, 714 (1947).

the ratio of P and P+1 does not change very much whether a compound contains a deuterium or not.[8]

The calculation may be exemplified as follows (Table 1).

Table. 1.

Mass number	107	108	109	110	111
AN*		100 (P)	7.38 (P+1)*	0.24 (P+2)*	
DAN*			100 (P)*	7.39 (P+1)*	0.24 (P+2)*
AN		100 (P)	6.71 (P+1)		0.23
Reaction product (AN+DAN)		38.1	100	6.53	0.23

* These values are quoted from Ref. 8.

The mass number, 109, of the reaction product contains not only the parent peak of the deuterated adiponitrile, but also the P+1 peak of the pure adiponitrile.

Therefore, the strength based on only the deuterated adiponitrile can be calculated by a conventional proportion using the values cited above:

$$100 - 38.1 \times \frac{6.71}{100} = 97.4$$

The deuteration is determined from the next equation:

$$\frac{97.4}{38.1 + 97.4} \times 100 = 71.9\ (\%)$$

This method of calculation gives the percentage of a monodeuterated adiponitrile. Furthermore, it is sure that the method is suitable for this investigation, because the formation of the adiponitrile containing two deuterium atoms may be neglected; the simple calculation shows that the existence of this compound results in the measurement of a larger value than the 0.23 of the 111 peak.

The symbols used in this report have the following meanings:

$$\eta_{\mathrm{ADN}} = \frac{\text{formed adiponitrile (mol)} \times 2}{\text{consumed sodium (g atom)}} \times 100\ (\%)$$

$$\eta_{\mathrm{PN}} = \frac{\text{formed propionitrile (mol)} \times 2}{\text{consumed sodium (g atom)}} \times 100$$

Results and Discussion

When a mixture of β-chloropropionitrile and acrylonitrile was treated with a sodium amalgam in the presence of water, the same products as those reported by Knapsack, namely, adiponitrile as the main product, and propionitrile, acrylonitrile, polymers of acrylonitrile, and organomercuric compounds as by-products, were obtained. These products were explained by him as being produced through the radical mechanism described above. However, the possibility of the mechanism could be eliminated because of the fact that hydroquinone added to the reaction solution did not disturb the reaction (Fig. 1). Therefore, the addition of β-chloropropionitrile to acrylonitrile with a sodium amalgam was dealt with in detail in order to clarify the reaction mechanism.

In the above-mentioned reaction, the water, added over a range of 0 to 1.0% by weight based

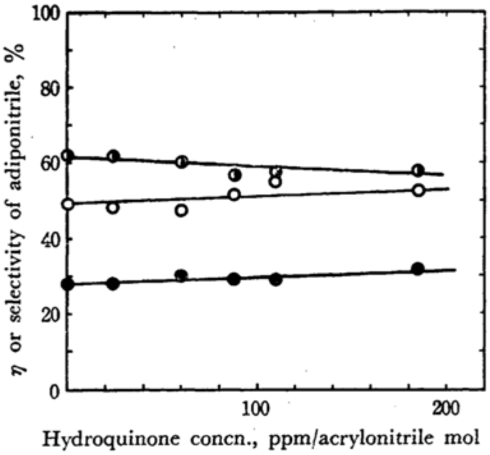

Fig. 1. The effect of hydroquinone.
○ η_{ADN}, ● η_{PN}, ◑ Selectivity of adiponitrile = ($\eta_{\mathrm{ADN}}/\eta_{\mathrm{ADN}}+\eta_{\mathrm{PN}}$)
Reaction conditions: β-chloropropionitrile, 0.3 mol; acrylonitrile, 0.2 mol; water, 0.5 wt%; temp., 40°C; time, 80 min

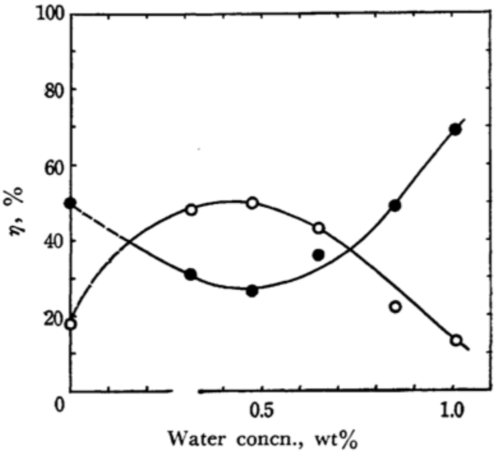

Fig. 2. The effect of water on efficiency of amalgam.
○ η_{ADN}, ● η_{PN}
Reaction conditions: β-chloropropionitrile, 0.3 mol; acrylonitrile, 0.2 mol; temp., 40°C; time, 80 min

A little amount of water (0—0.1 wt%) produces so much organomercuric compounds that the exact efficiencies are difficult to be obtained.

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[8] R. M. Silverstein and G. C. Bassler "Spectrometric Identification of Organic Compounds," 2nd, Johon Wiley & Sons. Inc., New York, (1963), p.p. 37, 38.

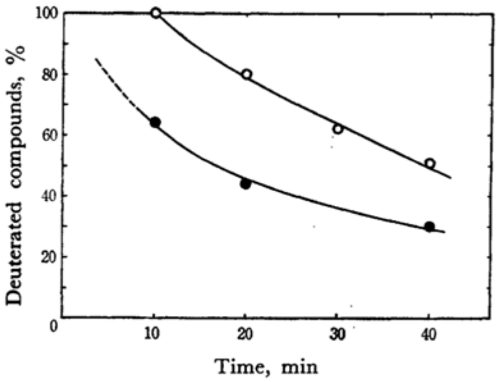


Fig. 3. Deuterations of adiponitrile and propionitrile.
○ deuterated adiponitrile
● deuterated propionitrile
Reaction conditions: β-chloropropionitrile, 0.3 mol; acrylonitrile, 0.2 mol; D_2O, 0.5 wt%; temp., 40°C

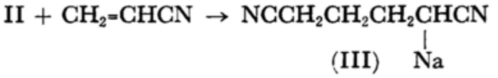
on the reaction solution, changed the η_{ADN} and η_{PN} values considerably (Fig. 2). To clarify the effect of water further, the deuterated water was added to the reaction solution in place of the water. The resulting adiponitrile and propionitrile were deuterated, whereas the reagents, such as β-chloropropionitrile and acrylonitrile, were not deuterated.

Figure 3 shows the correlation of the deuteration with the time. The deuteration of adiponitrile was 100% for the first ten minutes, after which it gradually decreased, while that of propionitrile decreased from the beginning of the reaction. The fact that deuterated compounds are obtained may mean that the water plays an important role as a proton donor and that some water is gradually formed during the reaction and then takes part in it, resulting in the decrease in the amount of deuterated products with the time. On the basis of the above findings, the reaction process producing adiponitrile may be expressed by the following equations. β-Chloropropionitrile reacts with a sodium amalgam to produce a cyanoethyl radical(I):

$$ClCH_2CH_2CN + NaHg \rightarrow \underset{\text{I}}{\dot{C}H_2CH_2CN} + NaCl + Hg \qquad (1)$$

As a free radical is detected by a ESR spectrometer in a similar reaction, using methyl acrylate and methyl β-chloropropionate in place of acrylonitrile and β-chloropropionitrile[9] respectively, Eq. (1) is also adequate for this reaction. As estimated in the report that an acrylonitrile radical in a solution easily initiated the polymerization of acrylonitrile,[10] only a little of the cyanoethyl radical (I) may exist in the solution. Polyacrylonitrile was produced in this dimerization. However, relatively little of the polymer was formed, and the formation was suppressed by the addition of hydroquinone. However, hydroquinone did not disturb the desirable reaction, namely, the formation of adiponitrile. Therefore, as is generally understood, almost all the hydroquinone added may be surmised to dissolve in the reaction solution, little remaining on the surface of the amalgam. Thus the desirable reaction is disturbed little. In other words, the cyanoethyl radical (I) seems to attach to the surface of an amalgam and diffuses little into the solution, thus making it suitable for the dimerization. The compound I, then, reacts with another sodium atom to produce a cyanoethyl sodium compound (II).

$$I + NaHg \rightarrow \underset{\text{(II)}}{NaCH_2CH_2CN} + Hg \qquad (2)$$


$$II + CH_2{=}CHCN \rightarrow \underset{\text{(III)}}{NCCH_2CH_2CH_2\underset{\displaystyle Na}{\underset{|}{C}}HCN} \qquad (3)$$

Equation (3) is an example of the Schorigin reaction, which involves the addition of the organometallic compound to the unsaturated bonds, such as C=C, C=O, and C≡N.

The compound III may produce adiponitrile by a protonation reaction, as is generally accepted in the reaction of an organometal σ-complex with a proton, the added water acting as a proton donor.

$$III + H_2O(\text{or } D_2O) \rightarrow NC(CH_2)_4CN(\text{or } NC(CH_2)_3CHDCN) + NaOH(\text{or } NaOD) \qquad (4)$$

$$NaOH + ClCH_2CH_2CN \rightarrow CH_2{=}CHCN + H_2O + NaCl \qquad (5)$$

This theory is supported by the formation of deuterated adiponitrile ($NCCH_2CH_2CH_2CHDCN$). The deuterated position was determined by a mass spectrometer. The peak of the mass number 41 was considerably higher in the case of the deuterated adiponitrile than in that of adiponitrile, showing the existence of a CHDCN fragment. In addition, a little α-cyanoethyladiponitrile was formed during the dimerization reaction. These facts indicate that the α-carbon carried deuterium, that is, that contained sodium.

When a little water (usually 0.5 wt%) is present in the organic layer, the above steps proceed smoothly, because Eq. (5) holds and reproduces water as a proton donor, which then takes part in Eq. (4).

This is confirmed by independent experimental results and by the decrease in the deuteration with time (Fig. 2). Furthermore, two other mechanisms producing adiponitrile can be considered: (a) the

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[9] T. Osa, Doctorate thesis, Univ. of Tokyo, 112 (1967).
[10] K. Ziegler, *Angew. Chem.*, **61**, 168 (1949).

TABLE 2. CODIMERIZATIONS WITH SOME VINYL COMPOUNDS AND THEIR HYDROCHLORINATED COMPOUNDS*

Raw material		Reaction products		
Hydrochlorinated compound	Polar vinyl compound	Wurtz dimer (%)	Schorign dimer (%)	Hydrodimer (%)
β-Chloropropionitrile	Ethylacrylate	Adiponitrile 0	Ethyl δ-cyanovalerate 39.8	Diethyll adipate 23.9
β-Chloropropionitrile	Methylacrylate	Adiponitrile 0	Methyl δ-cyanovalerate 29.1	Dimethyl adipate 30.4
Ethyl β-chloropropionate	Acrylonitrile	Diethyl adipate 1	Ethyl δ-cyanovalerate 11	Adipo-nitrile nitrile 5
Methyl β-chloropropionate	Acrylonitrile	Dimethyl adipate 3	Methyl δ-cyanovalerate 33.1	Adiponitrile 16.1

Reaction conditions:
hydrocholrinated compound, 0.3 mol; vinyl compound, 0.2 mol; temperature 40°C;
water 0.5 wt%/reaction mixture

* The yield was calculated from the assumption that 100% of amalgam was consumed within 80 min of the reaction time, even if all the amalgam was not used at 80 min.

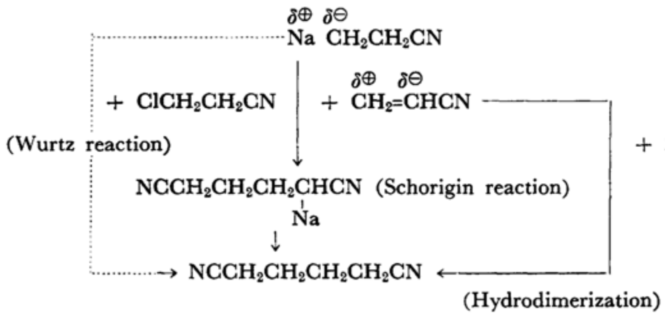


Fig. 4.

Wurtz reaction and (b) hydrodimerization. In the former reaction, the compound II reacts only with β-halogenopropionitrile, as is shown in Eq. (6):

$$\mathrm{II} + \mathrm{ClCH_2CH_2CN} \rightarrow \mathrm{NC(CH_2)_4CN} + \mathrm{NaCl} \tag{6}$$

In the latter one, on the other hand, acrylonitrile reacts with two protons and two electrons:

$$2\mathrm{CH_2{=}CHCN} + 2\mathrm{H^+} + 2\mathrm{e^-} \rightarrow \mathrm{NC(CH_2)_4CN} \tag{7}$$

The ratio of these three types of dimerizations was determined using several hydrohalogenated compounds and polar vinyl compounds. The results of these experiments are shown in Table 2. The above-mentioned dimerization was found to occur obviously in three types of reactions: 1) the Schorigin reaction (Eq. (3)), 2) the Wurtz reaction (Eq. (6)), and 3) hydrodimerization (Eq. (7)). The yield of products by the Wurtz reaction was lowest. In general, the Schorigin reaction may be considered to occur more preferably than the hydrodimerization.

In these reaction conditions, the compound II seems to attack acrylonitrile nucleophilically, because the β-carbon of acrylonitrile has a larger $\delta^{\oplus}$ charge than that of β-chloropropionitrile (Fig. 4).

Figure 2 showed that the formations of adiponitrile and propionitrile were competitive. Therefore, in order to obtain adiponitrile in a high yield, the water added must be suitably controlled. When water is added in an excessive amount, the propionitrile formation becomes the main process.

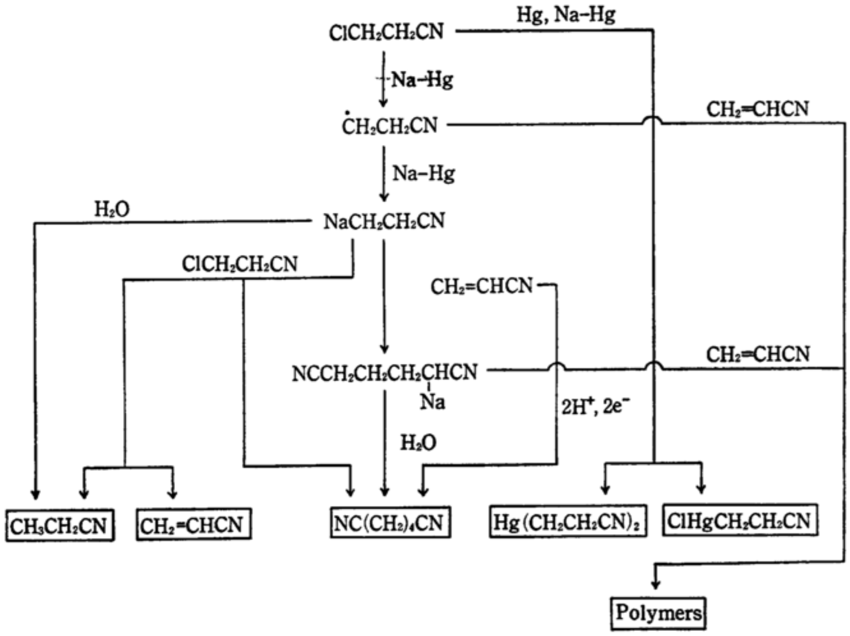
The increase in η_{ADN} with the addition of water in the range from 0 to 0.5 wt% suggests that the excess water participates in the reaction through Eq. (8):

$$\mathrm{II} + \mathrm{H_2O} \rightarrow \mathrm{CH_3CH_2CN} + \mathrm{NaOH} \tag{8}$$

The decrease in η_{PN} in the range between 0 to 0.5 wt% suggests that another reaction, such as Eq. (9), is predominant:

$$\mathrm{II} + \mathrm{ClCH_2CH_2CN} \rightarrow \mathrm{CH_3CH_2CN} + \mathrm{CH_2{=}CHCN} + \mathrm{NaCl} \tag{9}$$

Accordingly, the total reaction is as follows:



$$NaOH + ClCH_2CH_2CN \rightarrow H_2O + NaCl + CH_2{=}CHCN$$

Fig. 5. Reaction scheme.

$$2ClCH_2CH_2CN + 2NaHg \rightarrow NC(CH_2)_4CN + 2NaCl + 2Hg \qquad (10)$$

and

$$2CH_2{=}CHCN + 2H^+ + 2e^- \rightarrow NC(CH_2)_4CN \qquad (7)$$

Eq. (10) appears to be simply an example of the Wurtz reaction and does not show the role of acrylonitrile, because the acrylonitrile consumed by Eq. (3) is regenerated by Eqs. (5) and (9).

The polymers of acrylonitrile may be produced by the insertion reaction of III and the cyanoethyl radical diffused into the solution containing acrylonitrile:

$$\text{III} + nCH_2{=}CHCN \rightarrow \text{Polymers of acrylonitrile} \qquad (11)$$

$$\dot{C}H_2CH_2CN + nCH_2{=}CHCN \rightarrow \text{Polymers of acrylonitrile} \qquad (12)$$

The formation of organomercuric compounds may be explained by Eqs. (13) and (14):

$$ClCH_2CH_2CN + Hg \rightarrow ClHgCH_2CH_2CN \qquad (13)$$

$$2ClCH_2CH_2CN + 2NaHg \rightarrow Hg(CH_2CH_2CN)_2 + 2NaCl + Hg \qquad (14)$$

These reactions (11—14) waste the β-chloropropionitrile, sodium, and acrylonitrile.

From all these considerations, the following scheme (Fig. 5) may be proposed for this reaction. It is important that the formation of by-products shown in this scheme can be controlled by the preferable selection of additives. For example, when an adequate quantity of water is added, the formation of the organomercuric compounds can be completely suppressed, while the addition of hydroquinone can suppress the polymerization of acrylonitrile.

Consequently, adiponitrile was obtained in a yield of 50.1% (η_{ADN}) under these conditions; β-chloropropionitrile, 0.3 mol; acrylonitrile, 0.2 mol; water, 0.5 wt%; sodium amalgam, 0.5 wt% (0.1 g atom) of sodium; temperature, 40°C.

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