On the Oxidation of β-Aminopropionitrile. I

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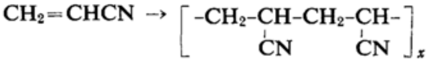
It is known that β-aminopropionitrile which can easily be synthesized from acrylonitrile and ammonia, turns to a viscous liquid and finally to a resinous solid, when it is stored in the air for a prolonged period. However, very little has been investigated on the polymerization of aminonitriles.

Akabori[1] proposed in his interesting theory of protein formation, that the protein-like polyamide would result from the polymerization of α-aminonitrile, $NH_2CH_2CN \rightarrow (-CH_2-CO-NH-)_x$. However he gave no experimental proof on his theory.

Whitmore and Mosher[2] have studied the polymerization of β-aminopropionitrile, and stated that the reaction proceeds according to the following scheme,

$$NH_2CH_2CH_2CN \rightarrow CH_2{=}CHCN + NH_3$$



$$CH_2{=}CHCN \rightarrow \left[\begin{array}{c} -CH_2-\underset{|}{\overset{}{CH}}-CH_2-\underset{|}{CH}- \\ \quad\quad CN \quad\quad\quad CN \end{array} \right]_x$$

where the reaction was initiated by the decomposition of β-aminopropionitrile into acrylonitrile and ammonia, then followed by the polymerization of acrylonitrile. However, it does not seem probable that the polymerization of acrylonitrile will occur in the presence of ammonia, since ammonia is known as a polymerization inhibitor. It is also unlikely that polymerization proceeded through a viscous product because polyacrylonitrile should precipitate from the reaction mixture, as it is not soluble in acrylonitrile, water and ammonia.

As our resinous product obtained from β-aminopropionitrile was found to be easily soluble in methanol, glacial acetic acid and formic acid, this material must be quite different from the polyacrylonitrile obtained by Whitmore and his co-worker.

This paper is to report on the result of our detailed investigation on the reaction products and the mechanism of polymerization reaction of β-aminopropionitrile.

It is well known, that the aliphatic amino group is easily oxidized to aldehyde. So that β-aminopropionitrile could be oxidized in an analogous manner and the resulting aldehyde may polymerize by aldol condensation according to the following reaction scheme;

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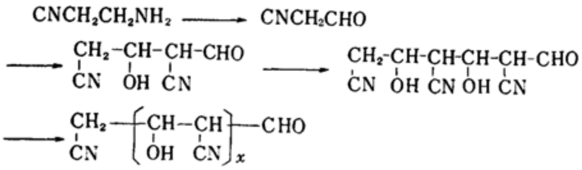
[1] S. Akabori, *Kagaku*, 25, 54, (1955).

[2] F. C. Whitmore and H. S. Mosher, *J. Am. Chem. Soc.*, 66, 725 (1944).



$$\mathrm{CNCH_2CH_2NH_2} \longrightarrow \mathrm{CNCH_2CHO} \longrightarrow \underset{\mathrm{CN}}{\mathrm{CH_2}}-\underset{\mathrm{OH}}{\mathrm{CH}}-\underset{\mathrm{CN}}{\mathrm{CH}}-\mathrm{CHO} \longrightarrow \underset{\mathrm{CN}}{\mathrm{CH_2}}-\underset{\mathrm{OH}}{\mathrm{CH}}-\underset{\mathrm{CN}}{\mathrm{CH}}-\underset{\mathrm{OH}}{\mathrm{CH}}-\underset{\mathrm{CN}}{\mathrm{CH}}-\mathrm{CHO} \longrightarrow \underset{\mathrm{CN}}{\mathrm{CH_2}}-\left(\underset{\mathrm{OH}}{\mathrm{CH}}-\underset{\mathrm{CN}}{\mathrm{CH}}\right)_x-\mathrm{CHO}$$

If this is the case, the resulting polymer may be acetylated and may give rise to the characteristic infrared absorption bands due to –OH and –CN groups. However, it was not successful to acetylate the polymer with various reagents, and no evidence for –OH or –CN was found from the infrared absorption spectrum of this compound as shown in Fig. 1. From these findings, it is believed that the polymerization reaction proceeds in a different way.

The colorless amorphous solid, obtained by treating the resinous polymer with anhydrous acetone to remove water and unreacted β-aminopropionitrile, was found to be very hygroscopic and to decompose at 120°C, resulting in the yellow mass which did not melt even above 250°C. The results of the molecular weight determination and the elementary analysis of this compound indicated the formular of $C_{12}H_{22}N_6O_5$ and the infrared absorption spectrum is shown in Fig. 1. As is clear from the spectrum, some differences were observed between the monomeric aminonitrile and the polymeric product.

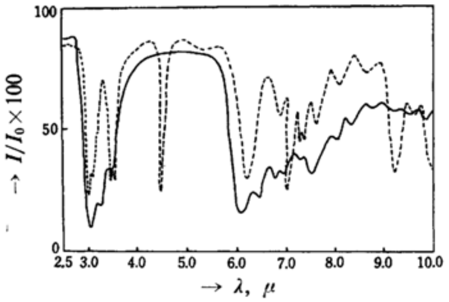


Fig. 1. Infrared absorption spectra.
---- β-Aminopropionitrile
—— Polymerization product

Two bands of N–H stretching vibration at 3.0 and 3.05 μ, splitted into three bands and shifted to 3.1, 3.3 and 3.4 μ. A band due to N–H bending vibration at 6.25 μ shifted to 6.45 μ, and a new band at 6.05 μ due to C=O stretching vibration appeared. These characteristic absorptions resembled very much those of the secondary amide such as *N*-methylacetamide which was investigated by Davis, Evans and Jones[3] as a model compound for polypeptides, and those of 6,6-Nylon. Therefore, it is very likely that this compound has a –CONH– linkage in its structure.

Regarding a new band at 6.70 μ, it is probable, that this band is due to the azoxy group. The reason for this assignment is that the position of this band coincided with that of the band arising from the stretching vibration of the azoxy group which was confirmed by Langley and others[4] in their infrared absorption study on azoxy compounds, such as 2-azoxy-2 : 5-dimethylhexane and ethyl 2-azoxybutylate.

Ultraviolet absorption spectra of these two compounds were also observed by the same authors, and their absorption maxima were reported as having two maxima at 223 and 280 mμ. The ultraviolet absorption spectrum of the polymer is also found to show two maxima at 215 and 275 mμ as shown in Fig. 2, and the locations of maxima are in good agreement with those of azoxy compounds if one considers the hypsochromic shift due to the use of water as a solvent.

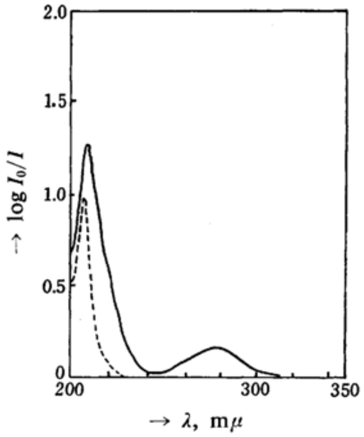


Fig. 2. Ultraviolet absorption spectra.
---- β-Aminopropionitrile
—— Polymerization product

In order to confirm the evidences of the azoxy group and –CONH– linkage in the polymer, the reduction of this compound was carried out, using concentrated hydrochloric acid and tin. The infrared absorption spectrum of the reaction product, which was obtained as colorless crystals, showed five bands at 5.85, 6.30, 6.70, 7.15 and 7.55 μ, as shown in Fig. 3, indicating the presence of amino acid, because these bands are characteristic of the hydrochloride of amino acid. And this supports the evidence of –CONH– linkage in the mother compound.

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[3] M. Davis, J. C. Evans and R. L. Jones., *Trans. Faraday Soc.*, **51**, 761 (1955).

[4] B. W. Langley, B. Lythgoe and N. V. Riggs, *J. Chem. Soc.*, **1951**, 2309.

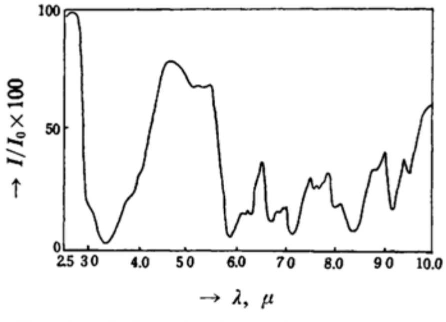
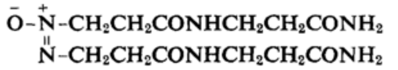


Fig. 3. Infrared absorption spectrum of reduction product of polymerization product.

Further investigation on the reduction product showed that the product was β-alanine and that this was obtained quantitatively by the reduction of the polymer. The presence of $-CONH_2$ group was also proved by the fact that ammonium chloride was found in the reduction products, and it was further confirmed that the nitrile group did not hydrolyze to $-COOH$ group during the reaction, because no metallic salt can be precipitated from the aqueous polymer solution.

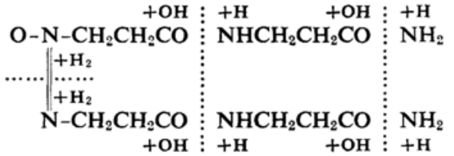
The presence of an azoxy group was also confirmed by the rapid evolution of gaseous nitrogen when the aqueous solution of the polymer was decomposed with sulfuric acid at room temperature. The fact that the aqueous solution of polymer was neutral, in contrast to the strong basicity of β-aminopropionitrile, indicated the polymer did not have a free amino group.

After considering above findings, the structure of resinous polymer obtained by standing β-aminopropionitrile in the air, is proposed as below;



$$\begin{array}{l}\overset{-}{O}\text{-}\overset{+}{N}\text{-}CH_2CH_2CONHCH_2CH_2CONH_2\\ \quad\ \| \\ \quad\ N\text{-}CH_2CH_2CONHCH_2CH_2CONH_2\end{array}$$

And the scheme of decomposition to yield β-alanine during the reduction may be shown as follows;



The rate of polymerization of β-aminopropionitrile was accelerated by adding small amounts of water and bubbling the air into the reaction mixture. The polymer thus obtained was found to be exactly identical to that obtained by standing the monomer in the air, and since one mole of ammonia and a small amount of hydrogen peroxide were formed from two moles of β-aminopropionitrile, the mechanism of this polymerization can be considered as the oxidation reaction accompanied by the evolution of ammonia in the presence of water as shown in Table I.

TABLE I. THE AIR OXIDATION REACTION

Nitrile g.	H_2O g.	Gas used	Gas blown l.	Product g.	NH_3 generated g.
15	0	Air	2800	No change	None
15	1.0	Air	560	White solid 15.0	1.80
15	3.8	Air	560	White solid 15.8	1.91
15	6.0	Air	720	White solid 15.1	1.87
15	1.0	N_2	2020	No change	None

Experimentals

1. Raw Material and Sample.—β-Aminopropionitrile was synthesized from acrylonitrile and aqueous ammonia according to Buc, Ford and Wise[5], and the fraction boiling at 86.3~87.0°C/21 mmHg was collected.

A polymeric sample was prepared by standing β-aminopropionitrile for two months in the air, followed by washing the resulting solid mass with anhydrous acetone to remove unreacted aminonitrile and water. A white amorphous and very hygroscopic solid was thus obtained, and dried in a vacuum. This sample decomposed at 120°C, yielding a product which did not melt above 250°C.

Found: C, 43.27; H, 6.69; N, 25.04%; mol. wt., detd. by freezing point depression using acetic acid. 311.1. Calcd. for $C_{12}H_{22}N_6O_5$: C, 43.63; H, 6.71; N; 24.22%; mol. wt., 330.4.

Ultraviolet absorption spectra were measured for the aqueous solution of 0.0651 g./l. A Shimadzu Model QR 51 spectrophotometer with 1 cm. quart celles was employed. Infrared absorption spectra were recorded with a Perkin Elmer Model 21 spectrophotometer on the sample film which was prepared by evaporating 2—3 drops of 3% methanolic solution on the sodium chloride window.

2. Reduction of Polymer.—Twelve grams sample was dissolved into 15 g. of water, and the solution was treated with 19.1 g. of metallic tin and 75 g. of 35% hydrochloric acid at 95~100°C for 10 hr. under stirring until the tin dissolved completely.

The resulting solution was diluted with four volumes of water and stannous ion was precipitated with hydrogen sulfide. The filtrate was concentrated under reduced pressure to get a crystalline product I which was found to be ammonium chloride.

After filtering it, the filtrate was subjected to further evaporation until one could get 16.5 g. of the second crystalline product II. The infrared absorption spectrum was measured on this material II using the potassium bromide pellet method.

The product II was then dissolved in a small amount of water and after neutralizing the solution with 1 N sodium hydroxide solution, it was boiled

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[5] S. R. Buc, J. H. Ford and E. C. Wise, *J. Am. Chem. Soc.*, 67, 92 (1945).

with an excess amount of freshly prepared cupric hydroxide. The hot filtrate was concentrated and cooled to get dark blue crystals. This was re-dissolved in water, and cupric ion was precipitated with hydrogen sulfide. When the filtrate was evaporated almost to dryness, a crystalline product III was obtained.

Found: C, 40.27; H, 7.86; N, 15.81. Calcd. for $C_3H_7NO_2$: C, 40.44; H, 7.92; N, 15.72%.

3. Decomposition with Sulfuric Acid.—According to Curtius procedure, 0.0818 g. of the sample was dissolved in 1.0 ml. of water and 1.5 ml. of 98% sulfuric acid was dropped into this solution with gentle heating. The evolving gas, collected over a 10% potassium hydroxide solution, measured 5.34 ml. As this gas was not absorbed by the alkaline pyrogallol solution, ammoniacal cuprous chloride solution or barium hydroxide solution, it was found to be pure nitrogen. The amount of nitrogen evolved was 8.17% per mole of the sample.

4. Determination of Neutralization Equivalent.—A solution of 0.0999 g. sample in 50 ml. of water was titrated with 0.1 N hydrochloric acid using methyl orange as an indicator. Neutralization equivalent was calculated as 951.4 from the titre of 1.05 ml. This value is considerably larger than that of β-aminopropionitrile (69.5), and the sample can be considered as almost neutral material.

5. Formation of Metallic Salts.—No precipitation was observed when barium hydroxide, cupric nitrate or silver nitrate solution was added to the aqueous sample solution.

6. Air Oxidation.—Decarbonated air or nitrogen was bubbled into β-aminopropionitrile in a 100 ml. reaction flask at the rate of 20 l./hr. The increase of viscosity and the rapid evolution of gas were observed during she introduction of air, which was continued until the content rapidly increased its viscosity, resulting in a resinous material. This product was treated with anhydrous acetone to remove unreacted β-aminopropionitrile and water, then it was dried under reduced pressure. The product was obtained as a very hygroscopic white amorphous mass.

Amount of ammonia evolved during the reaction, was determined by passing the gas into sulfuric acid, and the presence of hydrogen peroxide in the gas was detected by passing it into barium hydroxide solution, followed by the dissolution of the resulting white precipitate into hydrochloric acid, which turned to red with an addition of potassium iodide.

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