On the Oxidation of β-Aminopropionitrile. II

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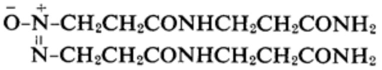
In the previous paper of this series[1], it was reported that β-aminopropionitrile became viscous and yielded a resinous material, when it had been stored in the air for a prolonged period. This resinous material was also obtained by bubbling air through β-aminopropionitrile and the following structure has been proposed for the oxidation product:



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

During the course of oxidation experiments, the evolution of a small amount of hydrogen peroxide was noticed. This phenomenon suggests that the oxidation reaction may be accelerated in the presence of hydrogen peroxide. The present work has been carried out to clarify the effect of hydrogen peroxide in the oxidation processes.

The effect of hydrogen peroxide on the oxidation of β-aminopropionitrile was investigated by means of ultraviolet absorption spectrum. As is shown in Fig. 1, the oxidation product similar to that in the air was obtained in the presence of 1 mol. of hydrogen peroxide per mole of β-aminopropionitrile. This result agrees quite well with that obtained from the infrared absorption measurement. Furthermore, the evidence that the oxidation product by hydrogen peroxide is the same as that in the air was also confirmed by the rapid evolution of gaseous nitrogen when this product was decomposed with sulfuric acid and by the formation of β-alanine when this product was reduced with tin and concentrated hydrochloric acid. It is understood from Table I, that 1 mol. of ammonia was evolved from 2 mol. of β-aminopropionitrile in the course of this oxidation reaction by hydrogen peroxide as was observed in the oxidation by air. Therefore, there results strongly suggest that the oxidation of β-aminopropionitrile by hydrogen peroxide proceeds through the same mechanism as that by air. At the mole ratio of 0.50 (hrdrogen peroxide/β-aminopropionitrile), a characteristic ultraviolet absorption spectrum was obtained, which may correspond to some intermediates of this oxidation reaction. Thus, ultraviolet absorption spectra were measured at different mole ratios.

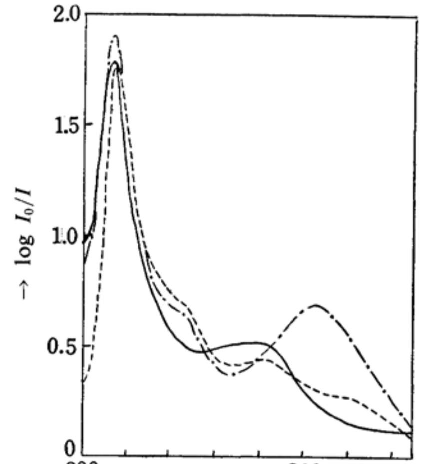


Fig. 1. Effect of mole ratios (H_2O_2/β-aminopropionitrile).

- · - Mole ratio 0.5
---- 〃 0.83
—— 〃 1.0

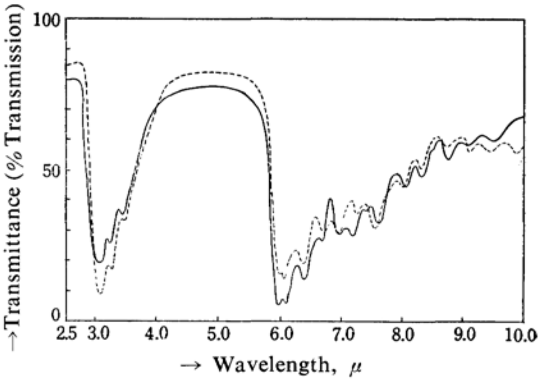


Fig. 2. Infrared absorption spectrum.

---- Air oxidation
—— H_2O_2 oxidation

It is understood from Fig. 3 that the spectra taken immediately after sampling show the presence of absorptions at 212∼215, 240∼242 and 307∼310 mμ regardless of their mole ratios. However, on standing for 48 hr., absorptions at 212∼215, 240∼242 and 307∼310 mμ were obtained only at mole ratios smaller than 0.7

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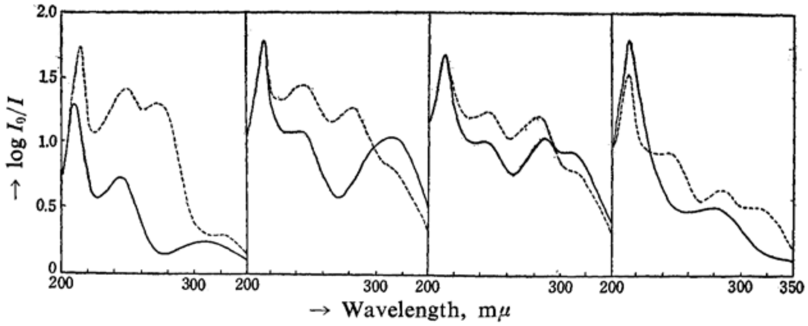
[1] T. Tachikawa, This Bulletin, 33, 1181 (1960).

TABLE I. NH_3 GENERATED

Nitrile g. used	25% H_2O_2 g. used	$\frac{H_2O_2}{\text{Nitril}}$ mole ratio	NH_3 generated g.	$\frac{\text{moles of } NH_3}{\text{moles of nitrile}}$
1.0	1.6	0.83	0.130	0.535
1.0	1.6	0.83	0.125	0.514
10.0	19.4	1.00	1.399	0.566



Mole ratio 0.1 Mole ratio 0.3 Mole ratio 0.7 Mole ratio 1.0

Fig. 3. Ultraviolet spectra of the reaction intermediates.

---- Immediately after sampling —— After 48 hr.

(hydrogen peroxide/β-aminopropionitrile), and at mole ratios greater than 0.7 an absorption at 280 mμ appears as an absorption at 307~310 mμ decreases.

Since several reaction intermediates were probably contained in a sample when measurements were performed right after sampling, it was not possible to postulate a reasonable reaction process and products. However it was inferred from the spectral measurements of samples which were allowed to stand for more than 48 hr. after sampling that the second reaction took place in the presence of 0.7 mol. of hydrogen peroxide against one mole of β-aminopropionitrile.

The mechanism proposed for the oxidation of β-aminopropionitrile is as follows:

1) In the first step of the oxidation reaction, β-aminopropionitrile is presumably transformed into β-hydroxylaminopropionitrile. This reaction process agrees with the known fact that an amino group is oxidized by hydrogen peroxide to yield a hydroxylamine group[2,3]. β-Hydroxylaminopropionitrile which was synthesized from hydroxylamine and acrylonitrile, was very unstable and transformed into a viscous substance in air. An infrared absorption spectrum of this viscous material showed six bands at 3.1, 3.35, 3.45, 6.05, 6.45, 6.75 μ, as shown in Fig. 4. This spectrum was similar to that of the oxidation product by air or hydrogen peroxide.

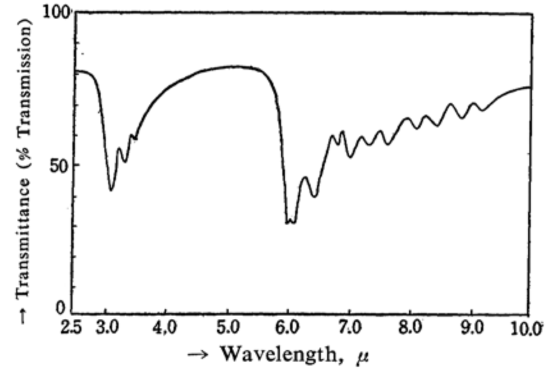


Fig. 4. Infrared absorption spectrum of the oxidation product of β-hydroxylaminopropionitrile.

2) At the next stage, β-hydroxylaminopropionitrile (or β-aminopropionitrile itself) may be hydrolyzed to yield β-hydroxylaminopropioamide (or β-aminopropioamide). This postulate is considered to be reasonable because a nitrile radical undergoes hydrolysis to produce an acid amide group in the presence of hydrogen peroxide as a catalyst[4].

3) An acid amide group thus formed reacts with a hydroxylamino group as the third step of the reaction. This reaction is well known as the reaction for the qualitative test of an acid amide group.

4) It is known that a hydroxylamino compound is a strong reducing agent and is oxidized

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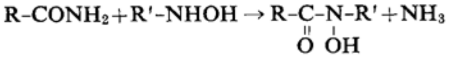
[2] L. Mamlock and R. Wolffenstein, *Ber.*, **33**, 159 (1900).

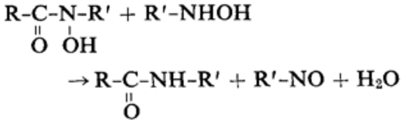
[3] R. A. Henry and W. M. Dehn, *J. Am. Chem. Soc.*, **72**, 2780 (1950).

[4] S. Soloway and A. Lipschiz, *Anal. Chem.*, **24**, 898 (1952).

to a nitroso compound. Therefore, a hydroxamic acid produced in the reaction process shown by Eq. 1 may be reduced to -CONH- group.



$$R\text{-}CONH_2+R'\text{-}NHOH \rightarrow R\text{-}\underset{\overset{\|}{O}}{C}\text{-}\underset{\overset{|}{OH}}{N}\text{-}R'+NH_3 \quad (1)$$



$$R\text{-}\underset{\overset{\|}{O}}{C}\text{-}\underset{\overset{|}{OH}}{N}\text{-}R' + R'\text{-}NHOH$$
$$\rightarrow R\text{-}\underset{\overset{\|}{O}}{C}\text{-}NH\text{-}R' + R'\text{-}NO + H_2O \quad (2)$$

5) The final product of this oxidation reaction is considered to be an azoxy compound. This final reaction process may be considered reasonable accordance to the work by Bamberger⁵⁾, who reported, that the formation of azoxy compound from a hydroxylamino compound has taken place with the evolution of hydrogen peroxide, assuming a nitroso compound as an intermediate.

The oxidation process mentioned above is formulated as follows:

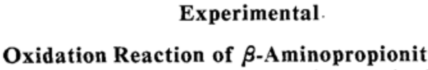
$$CNCH_2CH_2NH_2 + 1/2\ O_2(H_2O_2)$$
$$\rightarrow CNCH_2CH_2NHOH + (H_2O) \quad (3)$$

$$CNCH_2CH_2NHOH + H_2O$$
$$\rightarrow NH_2COCH_2CH_2NHOH \quad (4)$$

$$3NH_2COCH_2CH_2NHOH$$
$$\rightarrow \underset{(I)}{NH_2COCH_2CH_2NHCOCH_2CH_2NHOH}$$
$$+ NH_2COCH_2CH_2NO + NH_3 + H_2O \quad (5)$$

$$(I) + 1/2\ O_2(H_2O_2)$$
$$\rightarrow \underset{(II)}{NH_2COCH_2CH_2NHCOCH_2CH_2NO}$$
$$+ H_2O(2H_2O) \quad (6)$$

$$(I) + (II) + 1/2\ O_2(H_2O_2)$$



$$\rightarrow \overset{-}{O}\text{-}\overset{+}{N}CH_2CH_2CONHCH_2CH_2CONH_2$$
$$\overset{\|}{N}CH_2CH_2CONHCH_2CH_2CONH_2$$
$$+H_2O_2(H_2O+H_2O_2) \quad (7)$$

The secondary reaction process observed at higher mole ratios of hydrogen peroxide may be shown by Eq. 5 which corresponds to the reduction reaction by a hydroxylamino radical.

Experimental

Oxidation Reaction of β-Aminopropionitrile with Hydrogen Peroxide.—To β-aminopropionitrile (15 g.) which was placed in a 100 cc. three-necked flask equipped with a thermometer, a dropping funnel and a capillary, 25% hydrogen peroxide (29.3 g.) was added dropwise at below 5°C and at reduced pressure to removed ammonia gas as soon as it was reduced during the course of the reaction. The reaction was exothermic and ammonia gas was evolved violently as hydrogen peroxide was added to the reaction mixture. The reaction mixture become viscous as the reaction proceeded. After the addition of hydrogen peroxide was completed, the temperature of the reaction mixture was brought up to 90°C to remove water and β-aminopropionitrile unreacted. The yellow, amorphous, and hydroscopic solid (17 g.) was obtained from the residue, which decomposed at 120°C.

Found: C, 43.53; H, 6.25; N, 24.62. Calcd. for $C_{12}H_{22}N_6O_5$: C, 43.63; H, 6.71; N, 24.22%.

By means of the same method in the previous paper¹⁾, nitrogen gas (6.77 ml.) was evolved from this sample (0.1014 g.) by the decomposition with sulfuric acid and β-alanine (9.1 g.) was obtained from this sample (20 g.) by the reduction with tin (19.1 g.) and 35% hydrochloric acid (75 g.).

Found: C, 40.62; H, 7.65; N, 15.77. Calcd. for $C_3H_7NO_2$: C, 40.44; H, 7.92; N, 15.72%.

Ultraviolet Absorption Spectrum.—The Shimazu spectrophotometer model QR 51 equipped with a cell of 1 cm. path length was used throughout this work. Ultraviolet spectral measurements of the reaction intermediates were performed as follows: The 50% aqueous solution of β-aminopropionitrile (10 g.) through which nitrogen gas was bubbled was kept at below 5°C with stirring. After a known amount of hydrogen peroxide was added, nitrogen gas was introduced further into the reaction mixture and the ammonia gas which evolved was removed. Then, 0.01∼0.03 cc. of the reaction mixture was pipetted out and measured spectroscopically after dilution to 50 cc. with water. Samples which were allowed to stand for over 48 hr. were also measured, at which time the reaction stopped completely.

Infrared Absorption Spectrum.—A sample for the spectral measurement was prepared in the following procedure: A sample was dissolved in methanol to obtain 3% solution. Then, a piece of thin film was prepared on a cell by evaporating methanol from the solution. The infrared spectrum was obtained with a Perkin-Elmer spectrophotometer model 21 equipped with a sodium chloride prism.

Synthesis of β-Hydroxylaminopropionitrile.—Acrylonitrile (80 g.) is added slowly while cooling to about 10°C into freshly prepared solution of hydroxylamine (33 g.) in methyl alcohol. After being allowed to stand for two hours at room temperature the methanol and unchanged acrylonitrile are distilled off. The residue consists of a practically quantitative yield of β-hydroxylamino-propionitrile. It is a thick liquid which decomposes when distilled even under a pressure of a few millimeters of mercury. It is extremely sensitive to oxidation; it becomes viscous in the air. The colorless amorphous and hygroscopic solid was obtained by treating this viscous material with anhydrous acetone. An infrrared absorption spectrum was recorded with a Perkin Elmer spectrophotometer model 21 on the sample film which was prepared by evaporating 2∼3 drops of 3% methanolic solution on the sodium chloride window.

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5) E. Bamberger, *Ber.*, 33, 113 (1900).

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