Novel Preparation of Disodium Amidophosphate Hexahydrate, $Na_2PO_3NH_2 \cdot 6H_2O$, by the Reaction of Sodium *cyclo*-Triphosphate with Ammonia

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Synopsis. A reaction of sodium *cyclo*-triphosphate with ammonia at elevated temperatures gave water-insoluble sodium hydrogenamidophosphate, $NaHPO_3NH_2$. By treating the $NaHPO_3NH_2$ with a sodium hydroxide aqueous solution, disodium amidophosphate hexahydrate ($Na_2PO_3NH_2 \cdot 6H_2O$) was obtained.

It is well-known that amidotriphosphates are produced by the ammonolysis of *cyclo*-triphosphates in an aqueous solution.[1—3] The present authors tried to obtain them by the reaction of *cyclo*-triphosphates with ammonia. During the course of the reaction, however, water-insoluble sodium hydrogenamidophosphate ($NaHPO_3NH_2$) was obtained as the main product.

It was found in the present work that the obtained monosodium salt ($NaHPO_3NH_2$) could be converted to disodium amidophosphate by dissolving it in a sodium hydroxide aqueous solution. Although many reports have been published concerning the preparation of amidophosphoric acid and their salts,[4—7] it is claimed that the procedure reported here presents a novel process for the preparation of disodium amidophosphate hexahydrate ($Na_2PO_3NH_2 \cdot 6H_2O$).

Experimental

Sodium *cyclo*-triphosphate ($Na_3P_3O_9$) was prepared by heating sodium dihydrogenphosphate dihydrate ($NaH_2PO_4 \cdot 2H_2O$).[8] Five grams of the *cyclo*-phosphate were loaded into an autoclave (20 cm^3) equipped with a pressure gauge. Ten cm^3 of liquid ammonia was condensed in the autoclave, which was kept below −70 °C by a dry ice–acetone mixture, from a cylinder. The autoclave was then heated for 24 h in an electric furnace. After the reactions, the products were pulverized and subjected to further analyses.

Two-dimensional thin-layer chromatography (TLC) with alkaline and acidic solvents was used to identify the phosphate ions in the products.[9] The TLC cellulose plates (10×10 cm) were supplied by Funakoshi Chemical Co., Ltd. The color-development was carried out according to the technique reported in Ref. 10. The R_f values of the amido-,[5] amidotri-,[2] and *cyclo*-triphosphates[8] ions were given by preliminary TLC experiments. X-Ray powder diffraction patterns were obtained with Cu $K\alpha$ radiation. Phosphorus was determined colorimetrically.[11] Sodium was determined by atomic-absorption spectrophotometry. The nitrogen content was determined by using a Total Nitrogen Analyzer (Mitsubishi Kasei Kogyo Co., Ltd.). It is known that the phosphorus–nitrogen bonds are stable in alkaline aqueous solutions, but are broken under acidic circumstances.[2,4] The sample was dissolved in a 2 mol dm^{-3} sodium hydroxide aqueous solution and boiled for 30 min to remove any ammonia in the form of ammonium ions. The nitrogen present as amino groups ($N\text{-}NH_2^-$) was then determined. The nitrogen existing as ammonium ions ($N\text{-}NH_4^+$) was calculated by subtracting the $N\text{-}NH_2^-$ from the total nitrogen content (N-T).

Results and Discussion

Figure 1 shows a two-dimensional TLC chromatogram of the product obtained with the reaction at about 135 °C for 24 h. Assignments of the spots were made on the basis of the R_f values determined by the preliminary developments. The result shows the presence of amidophosphates in the product. About 5 g of the product was washed with three 20-cm^3 portions of water to remove water-soluble sodium *cyclo*-triphosphate and other soluble components. The thus-obtained water-insoluble product was air-dried. Its one-dimensional TLC chromatogram, developed with the alkaline solvent,[9] gave only one spot of the amidophosphate ion. Found: P, 25.97; Na, 17.15; $N\text{-}NH_4^+$, 0.65; $N\text{-}NH_2^-$, 11.36%. Calcd for $NaHPO_3NH_2$: P, 26.03, Na, 19.32, N, 11.77%. This result shows the water-insoluble product to be sodium hydrogenamidophophate, $NaHPO_3NH_2$.

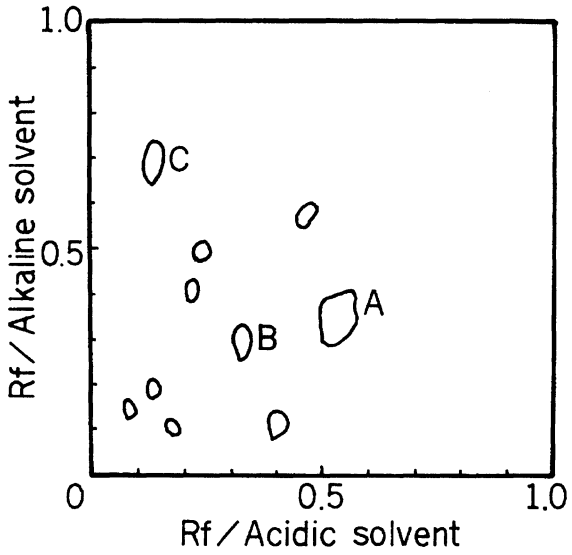

Fig. 1. Two-dimensional thin-layer chromatogram of the product of the reaction of sodium *cyclo*-triphosphate with ammonia at about 135 °C for 24 h. A: Amido-, B: amidotri-, C: *cyclo*-triphosphates.

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Upon dissolving in a sodium hydroxide aqueous solution, the monohydrogen salt ($NaHPO_3NH_2$) changed to disodium salt. A 2.5-g portion of the $NaHPO_3NH_2$ was dissolved in 30 cm^3 of a 10% (w/w) sodium hydroxide solution and filtered. Then, 120 cm^3 of ethanol was added to the filtrate at 0 °C. The precipitate (4.5 g) was dissolved in 30 cm^3 of water containing two or three grains of sodium hydroxide, recrystallized with 120 cm^3 of ethanol at 0 °C, and air-dried. Only one spot of the amidophosphate ion was found on the TLC chromatogram of the product obtained with the alkaline solvent.[9] The X-ray powder diffraction pattern of the product agreed with that of disodium amidophosphate hexahydrate ($Na_2PO_3NH_2 \cdot 6H_2O$).[12] Yield: About 1.5 g for 5 g of $Na_3P_3O_9$.

References

1) O. T. Quimby and T. J. Flautt, *Z. Anorg. Allg. Chem.*, **296**, 220 (1958).
2) W. Feldmann and E. Thilo, *Z. Anorg. Allg. Chem.*, **328**, 113 (1964).
3) W. Feldmann, *Z. Chem.*, **5**, 26 (1965).
4) H. N. Stokes, *Am. Chem. J.*, **15**, 198 (1893).
5) R. Klement and G. Biberacher, *Z. Anorg. Allg. Chem.*, **283**, 246 (1956).
6) M. Becke-Goehring and J. Sambeth, *Chem. Ber.*, **90**, 2075 (1957).
7) M. Watanabe, Y. Morii, and S. Sato, *Bull. Chem. Soc. Jpn.*, **57**, 2914 (1984).
8) e.g., Nippon-Kagaku Kai, "Muki-Kagobutsu No Gosei," in "Shin-Jikken-Kagaku Koza," Maruzen, Tokyo (1977), Vol. 8 (II), p. 493.
9) P. W. Schenk and K. Scheffler, *Z. Anorg. Allg. Chem.*, **356**, 56 (1967).
10) G. G. Berg, *Anal. Chem.*, **30**, 213 (1958).
11) D. N. Bernhart and A. R. Wreath, *Anal. Chem.*, **27**, 440 (1955).
12) JCPDS Card No. 16-540.