SHORT COMMUNICATION

Synthesis of Ethylenediamine labeled with Carbon-14

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Studies on the isotopic exchange of ethylenediamine with ethylenediamine complex have been initiated in this laboratory. In these studies, the synthesis of ethylenediamine labeled with isotopic carbon is required. Since radiocarbon is available in the form of barium carbonate, it is necessary to examine the procedures of preparation of ethylenediamine starting with the carbonate. The procedure which is employed in this laboratory is based on the following scheme.

$$Ba\overset{*}{C}O_3 \rightarrow K\overset{*}{C}N \rightarrow CH_3\overset{*}{C}N \rightarrow CH_3\overset{*}{C}H_2NH_2 \rightarrow$$
$$CH_3\overset{*}{C}H_2OH \rightarrow CH_2\overset{*}{C}H_2 \rightarrow CH_2BrC\overset{*}{H}_2\,Br \rightarrow$$
$$NH_2CH_2\overset{*}{C}H_2NH_2$$

By these steps the overall yield was about 20% of the theoretical value, based on barium carbonate.

Experimental

The methods of preparation of alkali cyanide from radioactive barium carbonate have been described by a number of authors; among those we adopted the method proposed by O. Simamura et al.[1] by which these authors obtained the highest yield up to 100%. Also, in our experiments the yield of the cyanide above 90% of the theory was confirmed. Radioactive silver cyanide was precipitated by adding the calculated amount of silver nitrate to the alkali cyanide solution which was obtained by the distillation of crude potassium cyanide in sufuric acid solution as usual.

About 200 mg. of radioactive silver cyanide was dissolved in a solution of 7.8 g. of inactive sodium cyanide in 12 ml. water. The solution was shaken at room temperature with 25 g. of methyl iodide in order to prepare acetonitrile. After about twenty to thirty hours' shaking the solution became homogeneous, and then the solution was slowly distilled, of which a fraction of 76–100°C was collected as crude acetonitrile. Hydrogenation was carried out at room temperature and atmospheric pressure with 50 ml. solution containing crude acetonitrile and 8 g. of Raney's nickel. The process adopted here to obtain ethylamine from sodium cyanide is similar to that performed by Kilmer and duVigneaud[2]. The filtered solution containing ethylamine was acidified and the yield of ethylamine was estimated by titrating with acid. Ethyl alcohol was obtained by the action of the calculated amount of sodium nitrite on the acid solution.

The dilute ethyl alcohol obtained by distillation of this solution was redistilled with calcium oxide by which ethyl alcohol was concentrated 80–90%. The yield of ethyl alcohol from sodium cyanide was about 60% of the theory.

The procedure of catalytic dehydration of ethyl alcohol consists in passing the vaporized alcohol through a tube which is packed with granules of alumina and maintained at the temperature of 360°C in an electric furnace. The reaction products were condensed in a trap cooled with liquid oxygen, and the whole system was evacuated to a few mmHg. After the dehydration process the trap containing ethylene was connected to a bromination apparatus. The bromination and the purification of the resulting ethylene dibromide were carried out in the usual way. The preparation of ethylenediamine from ethylene dibromide was made by the action of ammonia in a sealed tube. Five grams of the ethylene dibromide and 40 g. of concentrated ammonia (containing 35% NH_3 in weight) was sealed in the glass tube. By shaking the tube at the temperature of 50°C for seven hours the solution was made homogeneous, and then it was kept at the temperature of 50°C for twenty hours. The content of the tube was evaporated to dryness and distilled with alkali as usual to obtain ethylenediamine hydrate. Because of the scarcity

of the product, we cannot make an accurate measurement on the physical properties of the ethylenediamine monohydrate. However the obtained product was roughly identified by chlorine analysis on nhe ethylenediamine hydrochloride precipitated from the alcoholic solution.

Anal. Found: Cl, 54. Calcd. for $NH_2CH_2CH_2NH_2 \cdot 2HCl$: Cl, 53.4%.

The purity of the product was also certified by cation exchange resin, using 0.1 f. caustic soda eluant. The elution curve taken from the activity of the product just correspounds to the curve for the ordinary reagent of ethylenediamine. The yield of ethylenediamine from ethyl alcohol was 30% of the theory.

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1) M. Hasegawa, N. Inamoto and O. Simamura, This Bulletin, 28, 445 (1955).
2) G.W. Kilmer and V. duVigneaud, *J. Biol. Chem.*, 154, 247 (1944).