being diluted tenfold and saturated with hydrogen sulfide to eliminate antimony before chloride precipitation.

In the phosphorus oxychloride experiment, the low salt solubility led to low final measured activities. A reasonable calculation of exchange percentage was made, however, on the basis of the salt's final specific activity compared to its initial activity, its expected final activity being computed from the known reactant amounts.

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Low Pressure Reduction of Carbon^{14}-Labeled Barium Carbonate to Cyanide

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The conditions of reduction of carbon^{14}-labeled barium carbonate to carbon^{14}-labeled cyanide with zinc were investigated. A low pressure steel reaction vessel which allowed control of all variables was constructed and gave reproducible high yields of cyanide.

A number of syntheses of $NaC^{14}N$ from $BaC^{14}O_3$ have been described since 1941.[2-12] Initial attempts at synthesis followed the procedure of Jeanes,[11] according to which a boat containing a mixture of barium carbonate, sodium and zinc is placed in a Vycor train partially filled with iron wire and a stream of dry ammonia is passed through the tube for 4 hours at 650°. About twenty runs were carried out in this fashion; they showed a random distribution from 38 to 100% of the cyanide yields. After six or eight runs the Vycor tube usually cracked. It was therefore decided to devise a more reproducible procedure.

A systematic study of the influence of temperature on the yield of cyanide was first carried out. Since the end-product, zinc cyanide, is stable,[13] it was thought that the temperature at which the reduction occurs might be critical. The temperature reading was taken inside the Vycor train, directly above the boat containing the reactants. An iron–constantan couple was used, its insulation being replaced by narrow Vycor tubing. The control of the temperature was indeed the governing factor for a high conversion yield of cyanide from carbonate. A temperature change of 7% results in a 30% difference of yield. At a temperature of 640–650°, the yield of cyanide was 70%; at 655–670°, 90%; and at 670–680°, quantitative.

In order to control the temperature better and facilitate the carrying out of the final synthesis of C^{14}-labeled cyanide, a stainless steel vessel was constructed. The following procedure was arrived at after test runs with inactive barium carbonate: barium carbonate, an excess of zinc, and a catalytic amount of reduced iron powder[14] were mixed in a 12 × 80 mm. test-tube and the test-tube introduced into the reactor. Instead of gaseous ammonia, sodamide was used. The air was removed by flushing with a stream of dry ammonia and the vessel sealed and heated for 2 hours in a furnace to 680°. Six runs with inactive barium carbonate showed a 82–88% yield of cyanide. No cyanamide was formed. A blank run showed that no cyanide is formed in the absence of barium carbonate. Two runs with $BaC^{14}O_3$ were converted to silver cyanide. The specific activity was equal to that of the starting material.

Experimental

The reaction vessel had a volume of 20 ml. and accommodated a 12 × 80 mm. test-tube. The chamber was constructed to withstand a pressure of 140 atmospheres. The pressure during the reaction did not exceed 60 atmospheres. The outer dimensions were such that the bomb fitted into a Fisher Heavy-Duty combustion furnace. The oven was calibrated before the run to operate at exactly 680°. Power was supplied to the oven and series rheostat from a variable transformer for fine adjustment through a time switch for on and off regulation.

For each run about 0.75–1 mmole of barium carbonate was mixed in a small test-tube with 0.5–1 g. of zinc and about 10 mg. of iron powder reduced by hydrogen. The test-tube was transferred to the reactor which was then flushed with dry ammonia to replace the air and 15 mmoles of commercial sodamide was added. The head of the reactor was fastened tightly and the assembly placed in the cold oven and heated for 2 hours to 680°. After cooling the contents were washed out with water and the zinc powder removed by filtration. A few drops of $Ba(OH)_2$ were added for the precipitation of any unreacted carbonate which can be recovered by filtration. The volume of the solution did not exceed 25 ml. The hydrogen cyanide formed on acidification with 50% sulfuric acid was steam distilled in a micro-Kjeldahl apparatus. The yield of cyanide determined by argentimetric method was 82–88%. Two radioactive runs made with barium carbonate having a reported activity of 0.77 mc.[15] per millimole were analyzed. Found: (1) 124 mg. of $BaCO_3$ gave 69.2 mg. of AgCN (82% yield), with an activity of 0.76 mc. per mmole. (2) 148 mg. of $BaCO_3$ gave 88.5 mg. of AgCN (88% yield), with an activity of 0.78 mc. per mmole. Between runs the stainless steel vessel was cleaned with dilute nitric acid and dried. All traces of rust were removed with steel wool.

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