[CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Micro Syntheses with Tracer Elements. VI. The Synthesis of Silver Cyanate Labeled with C^{14} and of Urea Labeled with C^{14} and N^{15}[1]

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The reaction mechanism for the formation of potassium cyanate by the fusion of urea with potassium carbonate has been investigated. The fusion of urea with potassium carbonate-C^{14} has clearly shown that the cyanate carbon is contributed by the urea. Potassium cyanate-C^{14} and silver cyanate-C^{14} have been prepared. Ammonium-N^{15} cyanate-C^{14} has been prepared and has been converted to urea-C^{14}-N^{15} by Wöhler's reaction.

Although several reaction sequences are available, the synthesis of doubly labeled urea according to the following equations offers some advantages

$$K_2CO_3 + 2CO(NH_2)_2 \longrightarrow 2KNCO + CO_2 + H_2O + 2NH_3 \quad (1)$$

$$KNCO + AgNO_3 \longrightarrow AgNCO + KNO_3 \quad (2)$$

$$AgNCO + NH_4Cl \longrightarrow NH_4NCO + AgCl \quad (3)$$

$$NH_4NCO \longrightarrow CO(NH_2)_2 \text{ (Wöhler's Synthesis)} \quad (4)$$

In a preliminary experiment reaction 1 was carried out using $K_2C^{14}O_3$ and unlabeled urea. Since the resulting cyanate possessed no radioactivity, the cyanate carbon must be derived from urea. Accordingly, we began the synthesis with urea-C^{14}.[2]

Potassium cyanate-C^{14} was prepared by fusing urea-C^{14} and potassium carbonate according to the method described by Scattergood.[3] Whereas Scattergood reported almost quantitative yields of potassium cyanate when a 50% excess of urea was used, a study of the effect of varying the proportions of reactants was necessary in order to conserve labeled urea. A yield of 70 to 80% resulted when we used a 20% excess of potassium carbonate. The yields were determined by weighing the cyanate formed as silver cyanate.

Silver cyanate was converted to ammonium cyanate by treating a water suspension of the compound with the calculated amount of ammonium chloride, filtering off the silver chloride and diluting the filtrate with absolute alcohol. The ammonium cyanate was converted to urea by the method of Walker and Kay[4] without isolation from the solution.

Walker and Kay reported almost quantitative conversion of cyanate to urea and based their results on titration of the cyanate. In our experiments the highest yields of urea were never over 85% contaminated with 10–15% of biuret, the presence of which was not detected by these workers.

Experimental

(1) **C^{14}-Potassium Cyanate.**—In a Lawrence–Smith platinum crucible were intimately mixed 0.0720 g. (0.0012 mole) of C^{14}-urea and 0.0995 g. (0.0072 mole, 20% excess) of finely powdered anhydrous potassium carbonate. Fusion was started by heating the crucible near the top with a micro burner and allowing the conducted heat to initiate the fusion. This manner of heating minimized loss of urea by entrainment with evolved gases.

Reaction began with a rapid evolution of gases as soon as the urea melted. The mixture soon resolidified. The burner was then gradually moved toward the bottom of the crucible until the solid remelted to a clear quiescent liquid, whereupon heating was discontinued and the crucible was allowed to cool.

The melt was dissolved in 2 ml. of water and was then transferred into a 40-ml. centrifuge cone. The crucible was washed four times with 1-ml. volumes of water into the same cone.

The solution was treated with a slight excess of 0.1 *M* barium nitrate in order to precipitate the excess of carbonate originally added. The solution was first centrifuged then transferred into a second 40-ml. cone using a filterstick and suction. The barium carbonate precipitate was washed four times by triturating with 1-ml. portions of water, centrifuging, then filtering into the second cone with the filterstick as before.

The filtrates were treated with a slight excess of 10% silver nitrate. The mixture was cooled to 2–4°, centrifuged, and the liquid removed with the filterstick. The precipitate was treated six times with 1-ml. portions of water, followed by trituration, centrifugation and filtration.

The silver cyanate precipitate was dried and weighed. The yield was 0.1328 g. (74%).

(2) **C^{14}-N^{15}-Ammonium Cyanate and C^{14}-N^{15}-Urea.**—Into the centrifuge cone containing the 0.1328 g. of C^{14}-silver cyanate were added 10 ml. of distilled water and 0.0485 g. (0.009 mole) of $N^{15}H_4Cl$. The mixture was stirred continuously with a mechanical stirrer for 2.5 hours at such a rate as to keep the finely divided solids in suspension. The solution was then filtered into a 250-ml. flask using a filterstick and suction. The precipitate was washed ten times with 10-ml. portions of absolute ethanol and the washings were combined with the water solution by filtering with suction through a small buchner funnel into the 250-ml. flask. The flask, with the stopper tightly secured, was heated in an oil-bath at 48–50° for six hours.

At the close of the heating period the alcoholic solution was transferred quantitatively into a 250-ml. beaker and the liquid removed by evaporation. The dry residue was extracted with four successive 10-ml. portions of absolute methanol. The extracts were placed in a vacuum sublimator and the methanol was removed by evaporation. The product was sublimed at a temperature of 60–70° under a vacuum of 0.02–0.03 mm. The complete sublimation required six hours. The total yield was 0.0423 g. (58.5% based on urea used). The product melted over a range of 106–129° with a small portion melting at 160°.

Accordingly the sublimed urea was refluxed with 10 ml. of acetone. The solution was filtered, in order to remove a small amount of insoluble material, and evaporated to dryness. The colorless residue weighed 0.0382 g. (53.4% based on urea) and melted at 123–127°. The low melting point indicated that an impurity was still present. This impurity was removed by dissolving the compound in 6 ml. of hot anhydrous acetone, concentrating to a volume of 4.5 ml., cooling to −50° for 30 minutes, and then filtering off the mother liquor with the filterstick. The colorless product, after drying in a vacuum, weighed 0.030 g. (41.7%) and melted at 132–133°. The homogeneity of the product was checked by paper chromatography followed by a radioautograph. The product possessed a specific activity of 27 mg./mc. and contained 31% of N^{15}.

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(1) Work done under the auspices of the Atomic Energy Commission.

(2) A. Murray III and Anthony R. Ronzio, THIS JOURNAL, **71**, 2245 (1949).

(3) A. Scattergood, "Inorganic Syntheses," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1946.

(4) J. Walker and S. A. Kay, *J. Chem. Soc.*, **71**, 489 (1897).