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Short Communications

Synthesis of Bromoacetic Acid-1,2-^{14}C and Glycolic Acid-1,2-^{14}C

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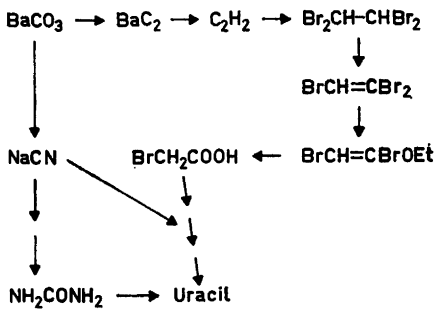
Ehrensvärd and Liljekvist[1] have developed a method for preparing uracil-2,4,-5,6-^{14}C on a small scale starting from barium carbonate-^{14}C of high specific radioactivity. The reported synthesis included the following reaction steps modified to enable work in the 100 μmole scale:



In the reaction series for the formation of uracil, bromoacetic acid-^{14}C is an intermediate. This compound, however, was not isolated and the optimal conditions for its synthesis were not investigated.

This communication will report some modifications in the reaction steps, leading to the formation of bromoacetic acid-^{14}C. Furthermore the isolation of bromoacetic acid-^{14}C will be described as well as its conversion to glycolic acid-^{14}C.

Preparation of barium carbide-^{14}C. In order to obtain a more reproducible yield of barium carbide-^{14}C from barium carbonate-^{14}C the following modification was used: Ether washed barium metal was pulverized with a file directly into a test tube previously flushed with argon. Barium carbonate-^{14}C was thoroughly mixed with the barium powder and a small piece of aluminium foil was pressed down on top of the mixture.

Hydrolysis of 1,2-dibromovinylethyl ether-1,2-^{14}C. Paper chromatographic analysis of the reaction products formed by the hydrolysis of 1,2-dibromovinylethyl ether-1,2-^{14}C showed the presence of bromoacetic acid-1,2-^{14}C and glycolic acid-1,2-^{14}C. Addition of hydrobromic acid (5 μl of 48 % hydrobromic acid) to the dibromovinylethyl ether prior to the hydrolysis diminished the formation of glycolic acid-1,2-^{14}C and promoted the complete hydrolysis. The temperature could be lowered from 110°C to 90°C without prolonging the reaction time, and the reduced temperature significantly improved the sealing of the bottom part of the apparatus during the reaction. Quantitative radioactive analysis of the reaction mixture after paper chromatography showed the bromoacetic acid-1,2-^{14}C to count for 85 % and the glycolic acid-1,2-^{14}C for 12.5 % of the total radioactivity.

Formation of glycolic acid-1,2-^{14}C. Bromoacetic acid-1,2-^{14}C in water solution is almost quantitatively converted to glycolic acid-1,2-^{14}C by standing overnight at 120°C in a closed vessel.

Isolation of bromoacetic acid-1,2-^{14}C. Bromoacetic acid is easily separated from glycolic acid by paper chromatography using ether-glacial acetic acid-water (13:3:1) as solvent. This method, however, was found to be very unsatisfactory depending on the small quantities and the high volatility of bromoacetic acid. A more suitable method is to add a siccative (sodium sulfate) to the reaction mixture and extract the formed paste with pentane. As the direct evaporation of the pentane caused big losses, benzene was added before this procedure. Evaporation of the pentane and most of the benzene gave a pure bromoacetic acid-1,2-^{14}C in benzene solution with only minor losses. The glycolic acid-1,2-^{14}C, remaining in the siccative paste, could be eluted with ethanol.

Yield. An average yield of seven syntheses gave 2 mC of bromoacetic acid-1,2-^{14}C (28 %) from 7 mC of barium carbonate-^{14}C, the formed product carrying twice the specific activity of the original barium carbonate-^{14}C (spec. act. 22.6 mC/mM).

1. Ehrensvärd, G. and Liljekvist, J. *Acta Chem. Scand.* **13** (1959) 2070.

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Quantitative Determination of Crystal Water and Moisture Content by Gaschromatography

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In the gaschromatographic determination of water some difficulties are encountered due to the polar nature of water and to the resulting tailing, to some absorption in the stationary phase, and to the affinity of water for the support. Rogozinski *et al.*[1] showed that in the direct determination by gaschromatography the detection limit for water in alcoholic solutions is about 10 %. The technique of adding water to the helium carrier gas to reduce tailing is described by Knight.[2] By fitting a gaschromatograph with a trapping arrangement to concentrate the moisture content in butane gas, Carlstrom *et al.*[3] were able to determine trace quantities of water. Smith[4] reports some observations in various stationary phases, and discusses the application of his method to quantitative analyses.

The use of indifferent substances such as Teflon-powder or Fluoropak as supports in gaschromatography of polar components has made possible the construction of columns which give a minimum of tailing.[5,6] When this communication was in preparation, Bennet[7] published a method describing the determination of water in organic solvents, using a column with Teflon-powder as a support, and Schwecke *et al.*[8] reported a way to determine moisture in food with methanol as a water extracting agent on Fluoropak support.

The present investigations were carried out for the determination of (1) crystal water in various compounds, and (2) the moisture content of hygroscopic and thermo-unstable substances. Methanol or acetone were used to extract water from the product to be analyzed, and the water content of the solvent was quantitatively examined on a column prepared by coating Teflon-powder with 20 % Carbowax 1500. Column temperature was 72°C and helium flow rate was 60 ml/min.

Experimental. A gaschromatograph, Perkin-Elmer 116 E, equipped with a hot wire detector, was fitted with an aluminium tubing, 6 mm × 2 m, packed with Teflon-powder (Perkin-Elmer 158–00–906) coated with 20 % Carbowax 1500. The stationary phase was dissolved in methylene chloride, slurried with the support and dried in a Rotavapor.* The new column was heated for 4 h at about 75°C and was then ready for use. It may be used for water determinations in acetone or methanol. The retention time acetone-water is 12 min and methanol-water 10 min at a temperature of 72°C and at a helium carrier gas flow rate of 60 ml/min. The water peak was symmetrical and sharp (Fig. 1).

The quantitative measurements of water in miscellaneous samples was accomplished in the following manner: a calibrated curve was obtained for 0–10 % water in methanol. (Acetone can also be used since the curve will be the same. However, methanol Merck *p.a.* is preferable to acetone Merck *p.a.* The former contains only 0.01 % moisture in a new opened bottle while the latter contains

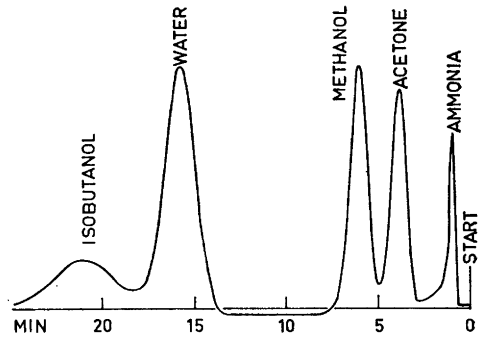

Fig. 1.

* The column is commercially available from Perkin-Elmer & Co, but is not difficult to prepare in the laboratory.