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NOTE

SYNTHESIS OF [^{14}C]PROPANE

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SUMMARY

[^{14}C]propane of high chemical and radiochemical purity has been prepared from [^{14}C]acetone via [1,3-^{14}C]acetone semicarbazone.

Key Words: [^{14}C]Propane, [^{14}C]Acetone, [^{14}C]Alkane, Acetone semicarbazone.

INTRODUCTION

Radiotracer techniques are being used in this laboratory (1) to investigate reaction pathways in the conversion of methanol to gasoline over the zeolite catalyst H-ZSM-5 (Mobil process). Such studies have required the production of specifically labelled oxygenates and hydrocarbons. We have previously reported the preparation of [methyl-^{3}H]methanol (2). The present communication outlines a synthetic method for the production of [^{14}C]propane. This is being used to investigate the methylation of propane to butanes by methanol over H-ZSM-5 as part of a study on the mechanism of hydrocarbon homologation on this catalyst.

A previous report (3) has outlined a route to ^{14}C-labelled n-heptane from the ketone using a Wolff-Kishner type reduction. The method we describe here is both simpler and more suitable for the preparation of a gaseous product.

[^{14}C]Propane was synthesised from [1,3-^{14}C]acetone in a two step synthesis. [1,3-^{14}C]acetone was converted to [1,3-^{14}C]-acetone semicarbazone (4) and then decomposed using a modification of the Wolff-Kishner reaction described by Huang-Minlon (5). In this modification potassium hydroxide was used in place of

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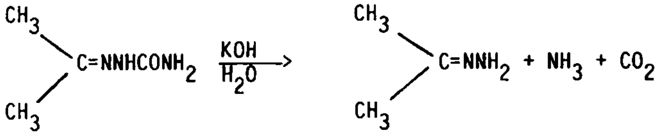
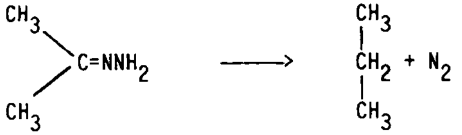
metallic sodium and the reaction time was shortened. This reaction is said to proceed in two steps:



.....1
(Ref 6)



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(Ref 7)

As the products of this synthesis were to be swept directly from the reaction vessel (i.e. without further purification) to an H-ZSM-5 catalytic convertor, it was important to retain any potential catalyst poisons such as amines and/or ammonia in the reaction tube.

EXPERIMENTAL

(a) [1,3-^{14}C]Acetone was supplied by Amersham International plc, England, in a glass break-seal ampoule (borosilicate glass) sealed under vacuum. The samples contained 1 mCi in 2.4 mg.

(b) Synthesis of [1,3-^{14}C]Acetone Semicarbazone was performed in a pyrex glass manifold constructed so that the [^{14}C]acetone (3 µl) could be diluted by the addition of unlabelled acetone (500 µl) before being vapour transferred into four break-seal ampoules (5 ml) and sealed.

A solution of semicarbazide hydrochloride (0.2 g, 0.0018 moles) and sodium acetate (0.23 g, 0.0023 moles) in water (1 ml) was prepared, attached to a second glass manifold, and the above acetone mixture (125 µl) vapour transferred into it. The reaction mixture was sealed off and allowed to warm to room temperature, resulting in the formation of a white, crystalline precipitate. The mixture was allowed to stand for ca 12 hours before the crystals were filtered off and washed with cold water (ca 20 ml). The yield of [1,3-^{14}C]acetone semicarbazone was 50 % (0.1 g).

The product was dissolved in ethanol (4 ml) for ease of handling. Its activity was determined by liquid scintillation counting and found to be 29.6 kBq/mg (0.8 µCi/mg).

(c) Synthesis of [1,3-^{14}C]Propane was carried out by adding a 1500 µl aliquot of the [1,3-^{14}C]acetone semicarbazone/ethanol solution to 200 mg ^{12}C-acetone semicarbazone and heating gently over a waterbath to dryness.

200 mg of powdered potassium hydroxide was loaded into a horizontally placed reaction tube (10 ml pyrex) followed by the semicarbazone and allowed to mix. One end of the tube was sealed. To neutralise any ammonia that may have formed by the decomposition of amines, a small drop of syrupy phosphoric acid was placed in this end of the tube, using a micropipette, without allowing it to come into contact with the reaction mixture. The tube was evacuated, sealed and placed in a tube furnace in such a way that the drop of phosphoric acid was outside the furnace. The tube was heated to 200 °C for 15 minutes to effect the conversion of the [1,3-^{14}C]acetone semicarbazone to [1,3-^{14}C]propane and allowed to cool.

Analysis of the reaction products was carried out by sweeping the contents of the reaction tube with helium (5 ml min^{-1}) through a sample loop connected to a GLC equipped for mass and radioactivity measurement. The yield of propane from the acetone semicarbazone was 21.5 % and the specific activity was 1.21×10^{-4} mCi $mmol^{-1}$. The main hydrocarbon impurities were methane (0.5 %) and ethane (0.8 %). The radiochemical purity was 98.3 %.

CONCLUSION

The method described above enabled the safe handling and conversion of [^{14}C]acetone into [^{14}C]propane. The high chemical and radiochemical purity of the product made it suitable for sweeping directly from the reaction tube into the H-ZSM-5 catalytic convertor without further purification. The semicarbazone method should easily be adopted to synthesis of other ^{14}C-labelled alkanes of high purity, being a particularly useful method for gaseous products.

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