

SYNTHESIS OF ^{14}C -CHLOROETHENE (VINYL CHLORIDE) AND ^{14}C -TRICHLOROETHENE

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Received on March 8, 1972.

SUMMARY

The synthesis of ^{14}C -chloroethene and ^{14}C -trichloroethene is described, the former in a state of high chemical purity suitable for polymerisation studies.

RESUME

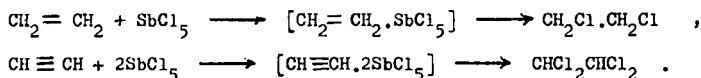
La synthèse de ^{14}C -chloroethene et de ^{14}C -trichloroethene est décrite, la première dans un état de haute pureté chimique convenant aux études de polymérisation.

INTRODUCTION

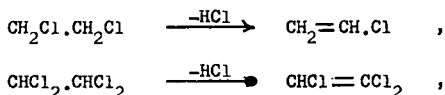
The availability of ^{14}C -chloroethene is important in studies of the polymerisation of chloroethene to the commercially important polymeric form. It is a necessary requirement that the monomer be of the highest chemical purity as slight traces of some contaminants, in particular, unsaturated species such as ethyne, can drastically change the polymerisation characteristics of the monomer. A sensitive measure of monomer purity may be found in the study of polymerisation rates, which increase with increasing monomer purity. The material we have synthesised shows polymerisation rates rather higher (~5%) than values reported (1) previously for the apparently pure monomer. In the case of ^{14}C -trichloroethene, chemical purity of the

order required for the ^{14}C -chloroethene is not required. In the context of chloroethene polymerisation, trichloroethene has been used as a transfer agent and studies on its incorporation into the polymer structures have been made.(2)

The route to both compounds utilises the method of Langguth.(3) Antimony pentachloride can be efficiently used to chlorinate certain unsaturated hydrocarbons, in this case, ethene and ethyne. The fully chlorinated product results, being formed via an unstable complex. This may be represented thus:



The chlorinated intermediates may then be readily dehydrochlorinated with base to give the chloroethenes, i.e.



using methods similar to that described by d'Allelio.(4)

While distillation as a method of purification of the final product is adequate in the case of the ^{14}C -trichloroethene, such was not the case with the ^{14}C -chloroethene. Highly pure chloroethene can be obtained by prepolymerisation followed by vacuum line distillation but losses are high and such a method is not applicable on the small scale used in radiochemical syntheses.

The method used for purification of the ^{14}C -chloroethene was preparative gas-liquid chromatography. Using a modified form of the Perkin-Elmer F21 preparative gas-liquid chromatograph which allowed radioactive substances, particularly combustion products from the flame-ionisation detector, to be safely vented to the outside atmosphere,(5) very high yields of gas-chromatographically pure material were obtained. The advantages of this method of purification are two-fold. Firstly, a high purity product can be obtained.

Polymerisation of the chloroethene reported here was shown by dilatometer measurements, (6) to be somewhat faster than any other reported chloroethene. Secondly, losses measured using this method are minimal, and it is a simple matter to manipulate very small amounts of material. The resulting overall chemical yields of ^{14}C -chloroethene and ^{14}C -trichloroethene were good, about 65% conversion from unsaturated hydrocarbon to final product being obtained.

Finally, it was found necessary to store the ^{14}C -chloroethene over an inhibitor, viz. 9,10-dihydroanthracene as the monomer underwent slow polymerisation even if kept at -35° , self-polymerisation occurring slowly under the initiating influence of the β -emission.

EXPERIMENTAL

Synthesis of Fully Chlorinated Intermediates.

(a) Pretreatment of Antimony Pentachloride

Antimony pentachloride was taken in a suitable round-bottomed flask fitted for magnetic stirring. The flask was incorporated into a high vacuum line ($< 10^{-4}$ Torr) and the antimony pentachloride degassed by three freeze-thaw cycles at -78° (not the more usual -196°) to allow removal of any free chlorine present in the antimony pentachloride. Failure to do this can lead to explosive reactions between ethyne and chlorine.

(b) Formation of chlorinated Intermediate

^{14}C -Ethene and ^{14}C -ethyne were obtained from the Radiochemical Centre, Amersham, and mixed with sufficient unlabelled material to give the required specific activity. Mixing was carried out using the high vacuum line and the usual break-seal technique. Homogeneity was ensured by successive condensation and evaporation of the mixed material in the break-seal tube originally containing the labelled material.

The diluted material was allowed to enter the flask containing the antimony pentachloride which was stirred vigorously until most of the hydrocarbon was absorbed, i.e. no further pressure drop was noted in the system. Remaining traces of non-absorbed material were removed by freezing and pumping leaving the reaction mixture containing the chlorinated product. The main contamination at this stage was antimony trichloride.

The mixture was then thoroughly degassed using freeze-thaw cycles at -78° and 36° , the mixture being homogeneous and more efficiently degassed at the higher temperature. Finally, the chlorinated material was distilled in the vacuum system using a trap cooled to -196° .

(c) Dehydrochlorination

(i) ^{14}C -1,1,2,2-Tetrachloroethane to ^{14}C -Trichloroethene

The crude ^{14}C -tetrachloroethane was treated with an excess of calcium hydroxide paste and heated under reflux for 2 hours. The excess calcium hydroxide was removed by addition of dilute hydrochloric acid and the organic layer washed with water and dried over anhydrous sodium sulphate. The product was finally distilled, the fraction distilling between 85° and 87° being collected.

(ii) ^{14}C -1,2-Dichloroethane to ^{14}C -Chloroethene

The ^{14}C -dichloroethene was dehydrochlorinated using an excess of 10% methanolic sodium hydroxide made by dissolving sodium hydroxide in the minimum amount of water and adding the appropriate amount of methanol. The crude ^{14}C -dichloroethane was added dropwise and the ^{14}C -chloroethene distilled via a reflux water condenser to prevent distillation of methanol and unchanged ^{14}C -dichloroethane. Small amounts of antimony oxychloride were also observed in the reflux condenser. The condensate of crude ^{14}C -chloroethene was collected in a trap cooled to -78° .

(d) Further Purification of ^{14}C -Chloroethene

The ^{14}C -chloroethene obtained above was further purified by gas-liquid chromatography using a Perkin-Elmer F21 preparative gas chromatograph fitted with a flame-ionisation detector and a 2 m column packed with 10% silicone grease (S.E. 30) on celite (60-80 mesh). Procedures to overcome the venting problem and a modified sample vessel (for use with very volatile materials) have been described elsewhere.(5)

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