A FACILE SYNTHESIS OF ^{14}C- AND ^{36}Cl-1,2-DICHLOROETHANE AND -1,1,2-TRICHLOROETHANE

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INTRODUCTION

The title compounds were needed for investigations forming part of a biological research programme in which this laboratory is engaged and which concerns the environmental impact of chlorinated hydrocarbons. The scale of most existing procedures (1-3) for the synthesis of the compounds is too large for our purposes. In addition, the synthesis of ^{14}C-1,2-dichloroethane described in the Journal of Labelled Compounds (4) seemed rather troublesome. We therefore designed an apparatus in which both DCE and TCE can be synthesized in a very simple way and on a small scale.

For the preparation of ^{36}Cl-TCE and ^{36}Cl-DCE $^{36}Cl_2$ was generated from Na^{36}Cl by addition of oleum to a solution of Na^{36}Cl in H_2O_2 (5).

To isolate and purify the compounds we used preparative GLC.

PROCEDURE

The procedure we developed has been derived from large-scale methods described in the patent literature. Figure 1. shows the apparatus used for the small-scale syntheses.

The addition of Cl_2 to ethene

$$Cl_2 + H_2C{=}CH_2 \xrightarrow{Zn/CCl_4} CH_2Cl\text{-}CH_2Cl$$

proceeds very fast and almost quantitatively in CCl_4 solution at room temperature in the presence of a trace of Zn powder, provided that the Cl_2 introduced has been thoroughly dried.

TCE was synthesized by radical chlorination of DCE:

$$CH_2Cl\text{-}CH_2Cl + Cl_2 \xrightarrow{h\nu} CH_2Cl\text{-}CHCl_2 + HCl$$

Equimolar amounts of DCE and Cl_2 yield about 70% of TCE contaminated with the by-products 1,1,2,2-tetrachloroethane and pentachloroethane and with a fairly large amount (25%) of unreacted DCE.

EXPERIMENTAL

1. Starting materials

^{14}C-ethene was purchased from NEN Chemicals GmbH in break-seal ampoules and Na^{36}Cl from RCC Amersham (250 μCi, 375 μCi/mM). The inactive chemicals used were of AR purity.

2. Synthesis of Dichloroethane-^{14}C

The break-seal ampoule with ^{14}C-ethene (2 mCi, 24 mCi/mM) was connected to A (figure 1), and a cylindrical vessel (volume 13.1 ml) with a stopcock to E. A 25 ml flask containing 0.4 ml of CCl_4 and 5 mg of Zn powder was attached to joint C. The flask was immersed in liquid nitrogen and the whole apparatus was evacuated. Stopcocks B and G were then closed, and the whole apparatus was filled with ethene, after which it was evacuated again, with stopcock F closed. This procedure was repeated three times. The last time tap H was closed before evacuation. Tap G was then closed, tap H opened, the break-seal broken, and finally, tap B opened. The diluted ^{14}C-ethene condensed very quickly in the reaction vessel. After 5 minutes tap B was closed. According to the same procedure, 16,0 ml of Cl_2 (from another cylindrical vessel)

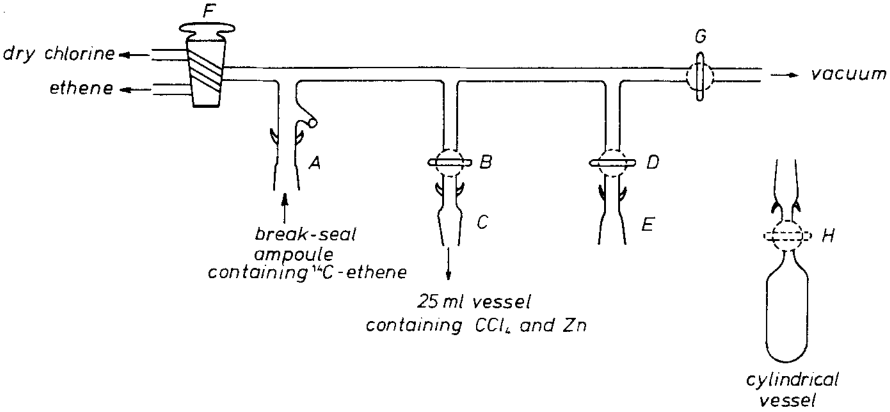

Figure 1

was also introduced into the reaction flask, after which the latter was immersed in a water bath (20 °C) while the mixture was magnetically stirred. Its greenish-yellow colour had vanished before it had reached room temperature. Stirring was continued for another 5 minutes, after which the mixture was frozen again. The contents of the reaction flask were allowed to warm up in a dry nitrogen atmosphere. In pilot experiments with inactive material we found that at this stage the ethene had reacted quantitatively (as shown by NMR with added $CHCl_3$ as the internal standard). Gas-chromatographic analysis showed that more than 99% of the product was DCE (contaminated with ca. 0.5% TCE). The ^{14}C-DCE was isolated by means of gas-chromatography (see Experimental 5). The chemical yield was 45.3 mg (67%), and the radiochemical yield 0.7 mCi (35%). This low radiochemical yield is probably owing to polymerization of the highly radioactive ^{14}C-ethene. The product was radiochemically pure ($>$ 99.5%, as checked by radio gas-chromatography).

3. Synthesis of ^{14}C-1,1,2-Trichloroethane

Two mCi of ^{14}C-ethene (4.84 mCi/mM) was diluted with 13.1 ml of inactive ethene. The ^{14}C-DCE needed for the synthesis of ^{14}C-TCE was prepared as described above. It was not isolated pure. Instead the volatile products were distilled (in vacuo) into a 25 ml flask attached to E. From the cylindrical vessel (25.1 ml) connected to A, another 25.1 ml of Cl_2 was introduced into the reaction flask. The contents of the flask were warmed to room temperature, and irradiated with a UV lamp (λ = 366 nm) for ten minutes, after which the solution had become colourless. After having been cooled with liquid nitrogen, the contents of the reaction flask were allowed to warm up in a dry nitrogen atmosphere.

In experiments with inactive material the composition of the reaction mixture at this stage was found to be:

TCE ca. 70%, DCE ca. 25%, 1,1,2,2-tetrachloroethane ca. 5%, other products $<$ 1% (data from NMR and analytical GC). ^{14}C-TCE was isolated by preparative GC.

The chemical yield was 75 mg (60%), and the radiochemical yield 0.9 mCi (45%) of analytically and radiochemically pure ($>$ 99.5%) ^{14}C-TCE.

4. Synthesis of ^{36}Cl-1,2-Dichloroethane and ^{36}Cl-1,1,2-Trichloroethane

Radioactive chlorine was prepared according to Woeber's method from $Na^{36}Cl$ (250 µCi) and H_2O_2/oleum(5) (nitrogen was bubbled through the solution). The chlorine gas (0.375 mM) was dried by passing it through a tube filled with P_2O_5 (Siccapent), after which it was trapped in a spiral tube with two stopcocks. When all the chlorine had been collected the trap was connected to A, and after evacuation of the trap and the whole apparatus, the chlorine was

distilled into a reaction flask containing CCl_4, Zn and ethene.
^{36}Cl-TCE was prepared according the procedure described for the synthesis of ^{14}C-DCE and ^{14}C-TCE. We isolated both the ^{36}Cl-TCE and its main contaminant DCE-^{36}Cl. The chemical yield of ^{36}Cl-TCE was 27 mg (55%), and that of ^{36}Cl-DCE was 5,3 mg (15%).
The fact that radiochemical yields were much lower (only about 30% of the activity was recovered), is probably due to exchange reactions with CCl_4. We had not foreseen the extensiveness of these reactions. It would probably be better, therefore, to carry out the preparative reactions without a solvent, and when they are complete, to distil the mixture into CCl_4.

5. Gas-Liquid Chromatography

The preparative GLC was performed on a 2 m x 1 cm column packed with Carbowax 20 M. The elution gas was nitrogen, and the column temperature 100 °C. For detection a catharometer was used. The fractions were collected in glass-traps, cooled in dry ice. Moisture was excluded with the aid of a tube filled with P_2O_5 (Siccapent).

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