

Preparation and analysis of isotopically pure tetratritiated methane

G. CIRANNI and A. GUARINO

Centro Nazionale di Chimica delle Radiazioni e Radioelementi del C. N. R.
Istituto di Chimica Farmaceutica e Tossicologica dell'Università, Rome, Italy
Received on 22 April 1966

SUMMARY

Many difficulties are encountered in the preparation of multilabelled compounds, as their purification and analysis for isotopic purity are involved. Another major problem is their self-radiolysis which can change their composition during storage.

This paper describes the preparation of CT_4 and the analyses which were carried out in order to check its purity: i.e. the mass spectrometric assay and a new gas chromatographic technique employing as detector an ionization chamber coupled with a vibrating reed electrometer. These analyses confirmed the isotopic purity of the CT_4 prepared, the main impurity being CHT_3 .

INTRODUCTION

There are many possible techniques by which to prepare hydrocarbons labelled with tritium; however, the preparation of multilabelled, isotopically pure compounds, as for example, CT_4 , $C_2H_4T_2$ etc. deserves special attention and requires highly accurate techniques of purification and analysis.

In the case of multilabelled alkanes it is necessary that all of the labelled molecules contain two (in the case of $C_2H_4T_2$) or four (in the case of CT_4) tritium atoms. They must however be diluted with inactive molecules to a specific activity of a few millicurie/mmole. Their use without dilution is prevented by a fast self-radiolytic decomposition. For example, a millimole of CT_4 contains ca. 116 curies.

In our laboratory we were interested in the preparation of these multilabelled compounds in order to investigate the chemical processes following the decay of a tritium atom bound to an organic molecule.

The synthesis and the use of $C_2H_4T_2$ in decay experiments have been reported elsewhere^(1, 2).

In the following pages the synthesis, purification and isotopic analysis of CT_4 will be described.

The preparation of CT_4 was carried out by the oxidation of tritium gas, on copper oxide, to isotopically pure tritiated water, and the subsequent reaction of the latter compound with aluminum carbide ⁽³⁾.

Special attention was paid to carrying out the reaction and to keeping the reactives and the reaction vessels as dry as possible; in fact, even a trace of water vapor adsorbed on the glass walls of the reaction vessels could produce the other isotopic methanes, CH_3T , CH_2T_2 and CHT_3 . In order to eliminate any water trace a sealed all-glass apparatus was employed and an extremely accurate high vacuum, high temperature outgassing of all the surfaces exposed to the tritiated water was performed. Since, however, even the extreme precautions taken could not ensure the isotopic purity of the CT_4 , it was of the utmost importance to check the isotopic composition of the methane obtained in order to estimate the percentage of the other methanes.

Two techniques were employed: a mass spectrometric analysis and a gas chromatographic analysis on a 44 m long glass capillary column, prepared and activated as described by Bruner and Cartoni ⁽⁴⁾. The latter analysis was performed at $-196^\circ C$, and the outlet of the column was connected to a flow ionization chamber to detect the tritiated species.

EXPERIMENTAL

CT₄ synthesis

Materials — Tritium, supplied by the Amersham Centre, England, had a stated 99.0% purity. The copper oxide was Merck Reagent Grade and the aluminum carbide was Reagent Grade obtained from Light Ltd. Products. The inactive hydrocarbons employed as carriers were Research Grade obtained from Rivoira and Co., Torino.

Preparation — The apparatus shown in Figure 1 was employed. The pyrex ampoules A (2.4 ml, containing ca. 40 mg of CuO) and C (2.4 ml, containing ca. 40 mg Al_4C_3) were outgassed under high vacuum for approximately 15 hours, at $450^\circ C$ and sealed. Then, these two ampoules were sealed to the main part of the apparatus. The ampoule B (ca. 7.6 ml), outgassed under heating at $450^\circ C$ at high vacuum, was filled with 4.5 C of pure tritium gas. All other parts of the apparatus were carefully outgassed in order to ensure the elimination of traces of water vapor. The apparatus was connected to the vacuum line with the ground joint D, and sealed off in G.

The break-seals of the A and B ampoules were broken with the corresponding magnetic hammers, embedded in glass, and the apparatus put into an oven at $400 \div 500^\circ C$, for two hours. After the reaction, in order to eliminate all traces of unreacted tritium, the apparatus was connected with the ground joint F to a vacuum line, cooled in a dry ice-acetone bath, and carefully outgassed after breaking the seal in I. The apparatus was then sealed in H, the seal

in C was broken and T_2O was allowed to react with Al_4C_3 at $100^\circ C$, in a water-bath, for two hours.

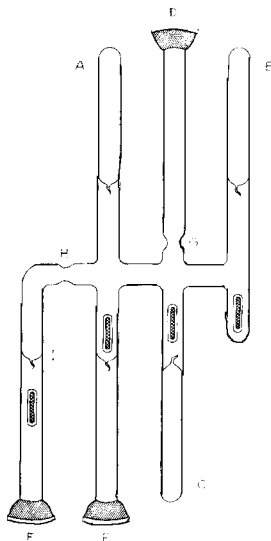


FIG. 1 — Apparatus used for the preparation of CT_4 .

Dilution and purification — The specific activity of CT_4 is ca. 116 C/mmole; in order to prevent its self-radiolysis, it was at once diluted with a large excess of inactive methane, up to ca. 24 mC/mmole. The traces of tritium were eliminated by bulb to bulb distillation using a trap containing activated 5 Å molecular sieves, cooled at $-160^\circ C$ (by means of a freon slush). The diluted methane- T_4 was washed with inactive hydrogen several times, and the other impurities — i.e. higher hydrocarbons — formed during the reaction, remained on the cooled trap. In order to complete the elimination of these impurities, inactive propane was added to the mixture, as a carrier, and the purified methane was recovered by Töpler pumping, taking the bulb at $-196^\circ C$.

Several checks of the chemical and radiochemical purity of the sample obtained were carried out by radio-gas-chromatography⁽⁵⁾. The following columns were employed :

- (i) 5 Å molecular sieves (2 m, i.d. 0.6 cm., $75^\circ C$, N_2 2 l/h) to identify traces of tritium, and C_2H_6 ;
- (ii) Activated silica gel (4 m, i.d. 0.6 cm., $95^\circ C$, A 1 l/h) to identify C_2H_2 , C_2H_4 and C_3H_8 ;
- (iii) Activated alumina with a 0.5% Silicone 550 (2 m, i.d. 0.6 cm, room temperature, A 0.5 l/h) in order to check the presence of higher hydrocarbons.

At the end of the purification cycle no detectable peak of tritiated compounds different from methane was recorded on the radio-gas-chromatograms.

A) *Mass spectrometric analysis* — A sample of CT_4 was analyzed in a mass spectrometer, model SP 21 F of Italelettronica Co., Rome.

The ratio of the ionic currents, due to the parent ions of CT_4 and CH_4 respectively, was found to agree, within the experimental errors, with the ratio deduced from the specific activity measurements. In addition, no contamination from the parent ions derived from CHT_3 , CH_2T_2 and CH_3T molecules could be detected. However, the extreme dilution of the CT_4 sample and the presence of the ions CT_3^+ , CT_2^+ , CT^+ from CT_4 made the analysis of other isotopic methanes quite difficult. It was therefore decided to use a more conclusive approach, i.e. a radio-gas-chromatographic technique.

B) *Gas chromatographic analysis* — The separation of CH_3T , CH_2T_2 and CT_4 was carried out by gas-solid chromatography with an adsorption glass capillary column. The column (0.22 mm i.d., and 47 m long) prepared and activated according to Bruner and Cartoni⁽⁴⁾ was employed at -196°C ; a mixture of He and N_2 was used as a carrier gas, at a flow rate of 1 ml/min. The effluent gases from the column were diluted with a stream of nitrogen at a total flow of ca. 20 l/h and passed through a 100 ml ionization chamber, coupled with a vibrating reed electrometer Cary mod. 32, and a chart strip recorder.

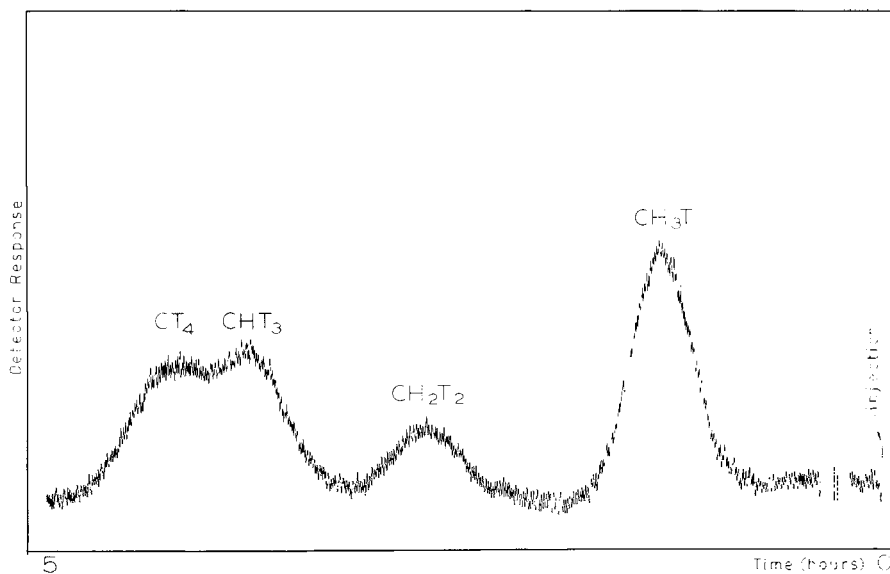


Fig. 2 — Isotopic gas chromatographic analysis of all tritiated methanes.

Figure 2 shows the separation achieved analyzing a sample containing all the isotopic methanes. Figure 3 gives the analysis of the sample of CT_4 prepared and purified as described. It may be seen that the main impurity is a trace of CHT_3 . The use of the CT_4 for the study of the reactions induced by the nuclear decay is reported elsewhere ⁽⁶⁾.

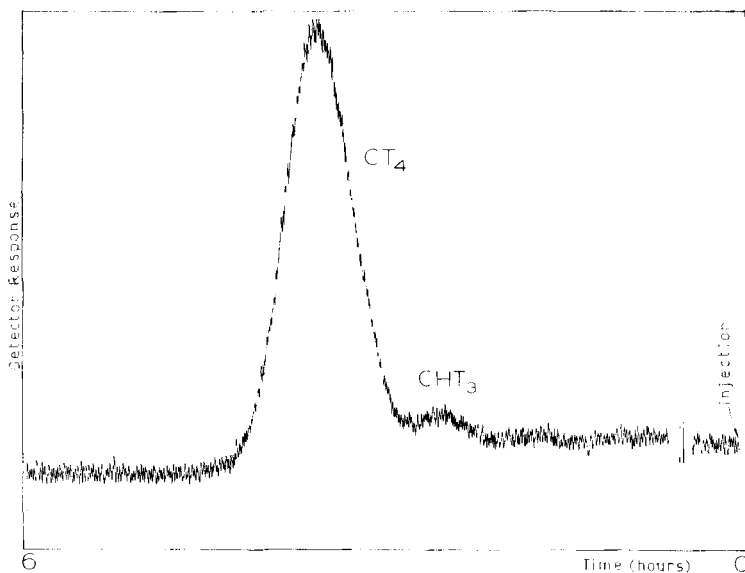


FIG. 3 — Isotopic gas chromatographic analysis of the prepared CT_4 .

ACKNOWLEDGEMENT

The authors wish to thank Prof. G. Giacomello for his continued help and useful discussions. They are indebted also to Dr. G.G. Volpi and to Dr. G.P. Cartoni for their help in the mass spectrometric and the gas chromatographic analyses respectively.

REFERENCES

1. ALIPRANDI B., CACACE F. and GUARINO A. — Proceedings of the Symposium on the Preparation and Biomedical Application of Labeled Molecules. EURATOM, Venezia, 1964, p. 35.
2. ALIPRANDI B., CACACE F. and GUARINO A. — Chemical Effects of Nuclear Transformations, Vol. II, I.A.E.A., Vienna, 1965, p. 470.
3. WHITE D.F., CAMPBELL I.G. and PAYNE P.R. — *Nature*, **166** : 628 (1950).
4. BRUNER F. and CARTONI G.P. — *J. Chromatog.*, **18** : 390 (1965).
5. CACACE F. and INAM-UL-HAQ — *Science*, **131** : 732 (1960).
6. CACACE F., CIRANNI G. and GUARINO A. — *J. Am. Chem. Soc.*, (1966, in press).