[CONTRIBUTION FROM THE SPECTROSCOPY LABORATORY, THE DOW CHEMICAL COMPANY]

The Preparation of Carbon Fourteen Labeled Methane and Carbon Tetrachloride

BY WILLIAM H. BEAMER

The need for carbon tetrachloride labeled with radioactive carbon-14 for several research problems has prompted the development of an efficient method for its synthesis. The starting material is barium carbonate supplied by the Isotopes Division of the Atomic Energy Commission with 3 to 4% of its carbon atoms radioactive. Since it is desired to obtain the organic compounds at this same high level of specific activity the preparation must be made on a scale of one to two millimoles. It is necessary to choose techniques which will permit the efficient handling of small amounts of gaseous or volatile compounds with minimum losses and yet give high reaction yields and a pure product. The all-glass vacuum line system in Fig. 1 was used. This system was mounted on a rack in a hood to minimize hazard to personnel in case of an accident liberating radioactive gaseous compounds.

The reactions used are

$$BaCO_3 + H_2SO_4 \longrightarrow BaSO_4 + CO_2 + H_2O$$

$$CO_2 + 4H_2 \xrightarrow[330°]{\text{Ni-ThO}_2\text{ catalyst}} CH_4 + 2H_2O$$

$$CH_4 + 4Cl_2 \xrightarrow{\text{light}} CCl_4 + 4HCl$$

These reactions were all tried in practice runs separately and then consecutively using non-radioactive materials.

The reduction of carbon dioxide with hydrogen is described by Sabatier and Senderens[1] and Pease and Chesebro.[2] The catalyst was prepared by absorbing nickel nitrate and thorium nitrate in 20 to 1 ratio in Silocel, a diatomaceous earth, about 8 to 16 mesh, roasting to the oxide and reducing with hydrogen at 330°. It was used many times without apparent loss of catalytic activity. Any carbon monoxide and excess hydrogen were burned to carbon dioxide and water by oxidation over copper oxide at 280° without oxidation of methane.

The analyses of the reaction products from the reduction step in non-radioactive runs were made by mass spectrometer. The yield of methane based on barium carbonate was 95 to 98% with a few runs as low as 90%. The methane contained 2 to 6% hydrogen, 1 to 4% unreacted carbon dioxide which was recoverable, 7% nitrogen and 0.1% argon. The nitrogen and argon were admitted unintentionally by an air leak in the hydrogen purification train. This was later corrected.

Various methods for carrying out the photochlorination of methane are described in the literature.[3,4,5] The direct chlorination in the gas phase with ultraviolet radiation seemed most applicable since only very small amounts of gas must be handled. The main requirement is that of quantitative conversion of methane to carbon tetrachloride with as little side product as possible. Some difficulty was experienced at first with the formation of hexachloroethane and other chlorinated ethanes and ethylenes. The procedure finally adopted gives about 1.5% hexachloroethane which can be separated from the carbon tetrachloride by vacuum distillation at low temperatures. The final product contained less than 0.1% hexachloroethane.

To completely chlorinate last traces of methylene chloride and chloroform it was found necessary to chlorinate in the liquid phase after vapor phase chlorination. A G-E type H-1 mercury sun-lamp was used.

Infrared analysis was made of the chlorinated products in non-radioactive runs. The early experiments gave about 0.1% of methylene chloride, 0.2 to 1.5% chloroform, 0.1 to 0.2% phosgene and 1 to 2% hexachloroethane. In the final runs by the method described here the analysis showed less than 0.1% of each of these impurities and a carbon tetrachloride purity greater than 99%. These figures represent the limits of the analytical method. The yield of carbon tetrachloride based on barium carbonate was 92 to 94%.

As a final check on the synthesis a preparation was made starting with barium carbonate containing a small amount of radioactive carbon. Carbon tetrachloride was synthesized and a part of it converted back to barium carbonate to obtain a radioactivity balance for the complete cycle. For this run 26.02 mg. of a radioactive barium carbonate preparation (I) were mixed with 529.3 mg. of ordinary barium carbonate (II). The carbon tetrachloride yield was 381.3 mg. or 92.5%. A 65.19-mg. sample of this product was quantitatively converted to barium carbonate (III) by combustion to give 83.42 mg. (theory, 83.64 mg.). This sample gave specific activities of 167.9, 167.5 and 168.3 counts/minute/mg. corrected to zero thickness of sample. The original (I) gave 3406 ± 2% counts/min./mg. at zero sample thickness. Calculation of the dilution with ordinary barium carbonate (II) gives 167.1 counts/min./mg. which agrees within 0.5% with (III).

Radioactivity measurements were made with a thin mica-window Geiger counter and Higin-

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[1] P. Sabatier and J. B. Senderens, *Compt. rend.*, **134**, 514 (1902); **134**, 689 (1902).

[2] R. N. Pease and P. R. Chesebro, THIS JOURNAL, **50**, 1466 (1928).

[3] Ellis, "The Chemistry of Petroleum Derivatives," The Chemical Catalog Co., New York, N. Y., 1934, p. 686, *et seq.*

[4] Bender, U. S. Patents 2,200,254 and 2,200,255.

[5] G. Egloff, R. E. Schaad and C. D. Lowry, Jr., *Chem. Revs.*, **8**, 1 (1931).

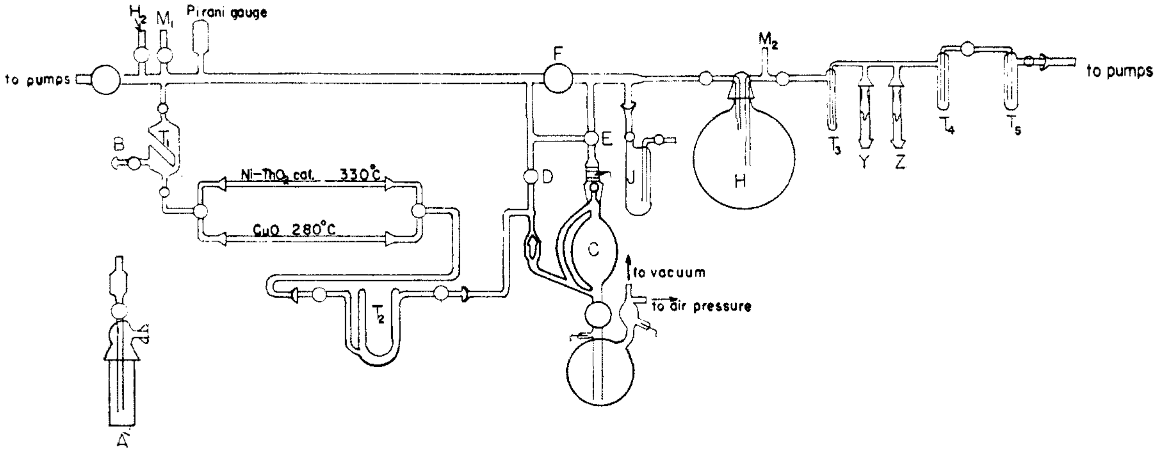

Fig. 1.—A, carbon dioxide generator; $T_{1,2,3,4,5}$, cold traps, T_4 and T_5 each consist of 4 small traps in series; C, Toepler pump; J, chlorine reservoir; H, chlorination flask; Y and Z, ampoules for product.

botham scaler. Carbon tetrachloride samples were weighed in sealed ampoules and oxidized in a modified Pregl-type combustion apparatus. The carbon dioxide was absorbed in sodium hydroxide and precipitated quantitatively as barium carbonate. The radiocarbon was assayed as thin layers of barium carbonate.[6,7,8]

Samples of strongly radioactive carbon tetrachloride made by this synthesis procedure were finally flame sealed in glass ampoules having a fragile break-seal and a ground joint.

Experimental

The barium carbonate is placed in the carbon dioxide generator A and attached to the system at B. The system is evacuated to less than 0.1 micron and the carbon dioxide liberated with concentrated sulfuric acid. Glass wool in the generator traps particles of barium carbonate which are scattered by the evolved gas. The generator is finally filled with acid and warmed to drive off last traces of gas. The carbon dioxide and water are condensed on the cold well T_1 containing liquid nitrogen and permanent gases are pumped off. The liquid nitrogen is later replaced with Dry Ice—acetone to trap water. Hydrogen which has been passed over platinized asbestos at 300°, soda lime and magnesium perchlorate is admitted to the system to a pressure about 100 mm. below atmospheric while the top bulb of the Toepler pump C is filled with mercury. The gases are circulated over the catalyst by the action of the Toepler pump with stopcocks D and F closed and E making connection from the top of the pump only to the system to the left of F. Water is trapped by Dry Ice–acetone in the Dewar-type trap T_2. The progress of the reaction is followed by the fall of pressure in the system indicated by the mercury manometer M_1. After the reduction is complete (about thirty minutes) the gases are circulated over the copper oxide to oxidize carbon monoxide and hydrogen. The reaction products are toeplered into the chlorination flask H (volume 1100 cc.) which has been previously evacuated. The pressure is read on the capillary manometer at M_2 and chlorine added from the vessel J in increments of about one tenth of the theoretical amount required. Intervals of five to ten minutes are allowed to insure complete reaction of the chlorine additions. Finally a 25% excess of chlorine is added and the irradiation continued for one hour. The incremental addition of chlorine is desirable to prevent the formation of explosive mixtures of methane and chlorine and to minimize the formation of hexachloroethane. The yield of chlorinated ethanes and ethylenes also increases with the intensity of the radiation.

After chlorination the reaction products are transferred to trap T_3 by vacuum distillation with liquid nitrogen. The hydrogen chloride and recoverable carbon dioxide are transferred successfully to T_4 and T_5 by the same procedure while holding the chlorinated methanes and some chlorine in T_3 with a Dry Ice—acetone bath. The mixture in T_3 is again irradiated to chlorinate last traces of methylene chloride and chloroform in the liquid phase. During this time T_4 is kept at about −40° to prevent the chlorine pressure from becoming greater than atmospheric. After about thirty minutes of irradiation the chlorine and hydrogen chloride are transferred to T_4 and T_5 by successive distillations and the mixture of carbon tetrachloride and hexachloroethane is frozen into ampoule Y. Ampoule Z is surrounded by Dry Ice–acetone and the carbon tetrachloride is distilled away from the hexachloroethane which is held in Y at 0°. This separation is clean cut as indicated by separate experiments. The two ampoules are sealed off with a flame.

Summary

Carbon radioactive methane and carbon tetrachloride have been synthesized on a one to two millimole scale from $BaC^{14}O_3$ with yields of about 96 and 93%, respectively. The purity of the carbon tetrachloride as indicated by analyses of trial runs is greater than 99%.

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[6] A. F. Reid, "Preparation and Measurement of Isotopic Tracers," J. W. Edwards, Ann Arbor, Michigan, 1946, p. 83.

[7] A. F. Reid, A. S. Weil and J. R. Dunning, *Anal. Chem.*, **19**, 824 (1947).

[8] W. G. Dauben, J. C. Reid and P. E. Yankwich, *ibid.*, **19**, 828 (1947).