[CONTRIBUTION FROM THE WALKER LABORATORY OF THE RENSSELAER POLYTECHNIC INSTITUTE]

A New Synthesis of Chloroform-*d*[1]

BY MASON H. EARING AND JOHN B. CLOKE

In the course of certain theoretical investigations now under way in this Laboratory, a convenient supply of heavy chloroform of known degree of purity became necessary. Although two preparations of this compound have been reported previously,[2] both employ chloral as one of the reactants. Since the deuterium exchange with chloral under the conditions employed has been reported to be appreciable,[3] it was believed that the action of deuterium oxide on anhydrous calcium trichloroacetate might lead to a better isotopic yield. The anhydrous salt, not reported previously, was prepared from air-dried calcium trichloroacetate by dehydration under diminished pressure.

$$(Cl_3C—CO_2)_2Ca + D_2O \longrightarrow 2DCCl_3 + CaCO_3 + CO_2$$

Experimental

Anhydrous Calcium Trichloroacetate.—A solution of calcium trichloroacetate, prepared by the careful neutralization of trichloroacetic acid with calcium carbonate, was filtered from excess carbonate and allowed to evaporate in a large dish. Fifty grams of the air-dried acetate was placed in a special type of "pistol" drier charged with phosphorus pentoxide and subjected to a vacuum of a few microns. At the end of 80 hours, and several replacements of drying agent, the product appeared to be anhydrous, since it failed to hydrate the phosphorus pentoxide visibly at 70° after several hours.

Half-gram samples of the product were analyzed for water by fuming them to dryness with sulfuric acid and weighing the ignited calcium sulfate. The product was thus found to contain less than 0.01 mole of water per mole of products and was considered to be anhydrous. By this method also, the air-dried salt was found to crystallize with three moles of water.

Chloroform-*d*.—A weight of 30 g. of anhydrous calcium trichloroacetate was placed in a 100-ml. flask and several small chips of metallic sodium added. Ten ml. of deuterium oxide d^{20}_4 1.1015 (0.969 mole fraction)[4] was added cautiously and the flask attached to an apparatus for automatic separation and return of the deuterium oxide (Fig. 1). The apparatus contained a minimum of joints and was fitted with a calcium chloride drying tube and a bulb to eliminate the effects of foaming which may occur toward the end of the reaction.

The reaction flask was immersed in a bath maintained at about 125° for 3 hours during which time 8.5 ml. of chloroform collected. After the removal of the chloroform, the bath temperature was raised and the remaining deuterium oxide removed. In this way 8.4 ml. of deuterium oxide was recovered. This corresponds to a 60% yield of chloroform-*d* based on the deuterium oxide consumed. The product was dried over calcium chloride and distilled. It boiled at 61.5° (uncor.).

Density, Refractive Index and Infrared Spectrum.—The density was determined in a 5-ml. pycnometer in a bath maintained at 20 ± 0.05°. The refractive index was measured in a Bausch and Lomb Abbe refractometer maintained at constant temperature by water from this bath; d^{20}_4 1.5007 (av. of nine determinations), n^{20}_D 1.4451 as compared with d^{20}_4 1.4887, n^{20}_D 1.4450 for ordinary chloroform measured under the same conditions.

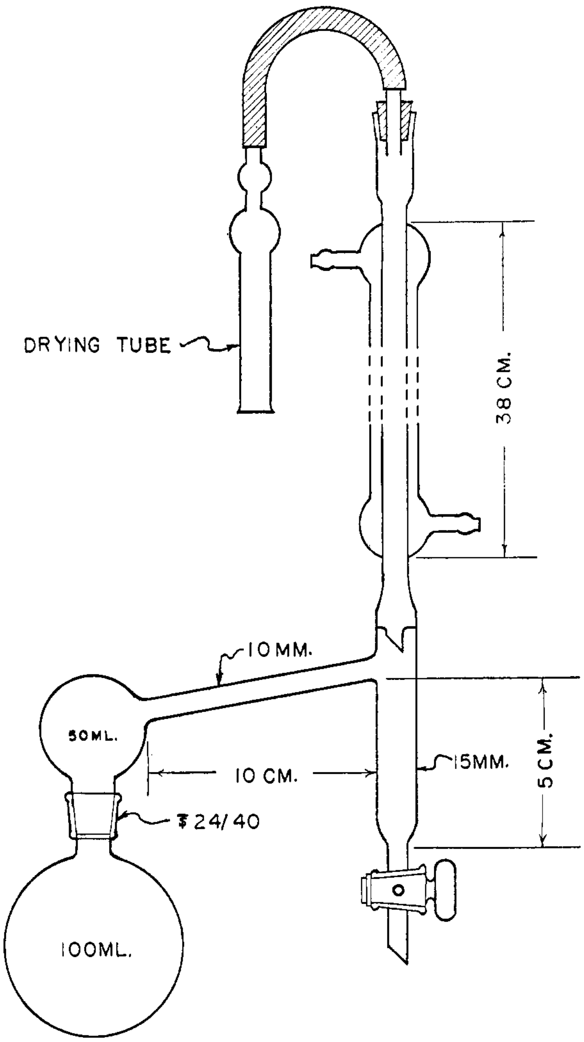

Fig. 1.

The infrared spectrum was measured with a Perkin-Elmer infrared spectrometer, Model 12-B, with Brown Instrument Company recorder, using a rock salt prism and cell windows. The graph in Fig. 2 was replotted from the recording with the omission of atmospheric water and carbon dioxide bands. Standard solutions used in the analysis for purity by infrared absorption were prepared by weighing out the appropriate amount of freshly distilled alcohol and water-free chloroform and diluting to 100 ml. with benzene. All measurements of per cent. transmission including that of the product were made in the same (0.025 mm.) cell.

Results

The infrared spectrum shows transmission minima occurring at 740, 908 and 2256 cm.$^{-1}$ corresponding to those observed in Raman spectra of chloroform-*d*.[2b,5] Other minima at 769, 1218

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[1] This paper is an abstract of the first part of a thesis presented by Mason H. Earing to the Rensselaer Polytechnic Institute for the degree Doctor of Philosophy. Presented before the Organic Division of the American Chemical Society at Philadelphia, April 13, 1950.

[2] (a) Breuer, THIS JOURNAL, **57**, 2236 (1935); (b) Truchet, *Compt. rend.*, **202**, 1997 (1936).

[3] Lauder and Wright, *Nature*, **158**, 381 (1946).

[4] Deuterium oxide (0.969 mole fraction). Value reported above calculated from density according to formula of E. Swift, THIS JOURNAL, **61**, 198 (1939).

[5] Wood and Rank, *Phys. Rev.*, **48**, 63 (1935).

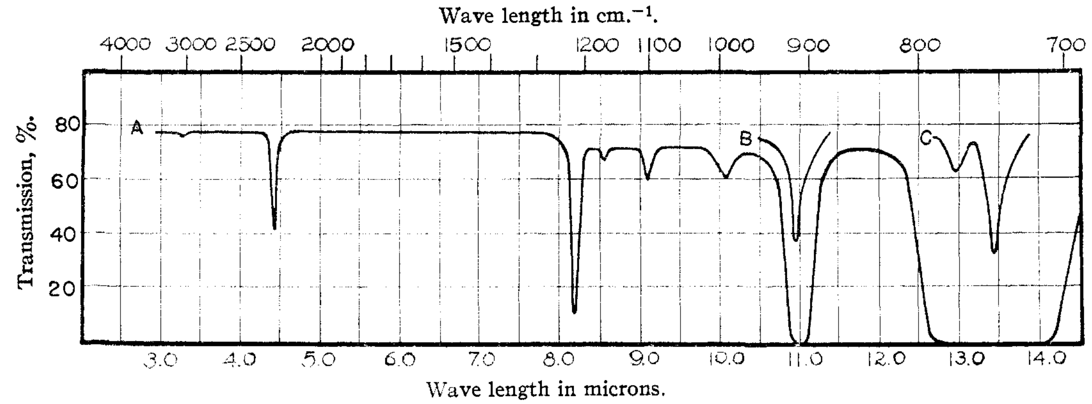

Fig. 2.—Infrared spectrum of product: curve A, liquid, 0.025 mm. cell; curve B, gas, sat. vapor, 10 cm. cell; curve C, gas, 60 mm. pressure, 10 cm. cell.

and 3030 cm.$^{-1}$ correspond to those reported for ordinary chloroform.[5,6] Several very weak minima occurring at 991, 1097 and 1171 cm.$^{-1}$ possibly result from combinations of the fundamentals.

Since the minimum at 1218 cm.$^{-1}$ appeared to persist even in low concentrations of ordinary chloroform, it was decided to use this minimum as a basis for the quantitative analysis of the product. The standard solutions of chloroform in benzene possessed a minimum at this point and obeyed the Beer–Lambert law, as observed in Fig. 3. Transmission of the product (dotted line) corresponded to 6.1 g. of ordinary chloroform in 100 ml. of product or to a 0.960 mole fraction of chloroform-*d*. The average deviation as estimated from the results of three determinations was 0.008 mole fraction units.

Assuming equimolar volumes, the observed density increment of the product as compared to the calculated corresponds to a 0.952 mole fraction, in good agreement with the above analysis.

Acknowledgment.—The authors are indebted to Mrs. Mason H. Earing for preparation of the line drawings.

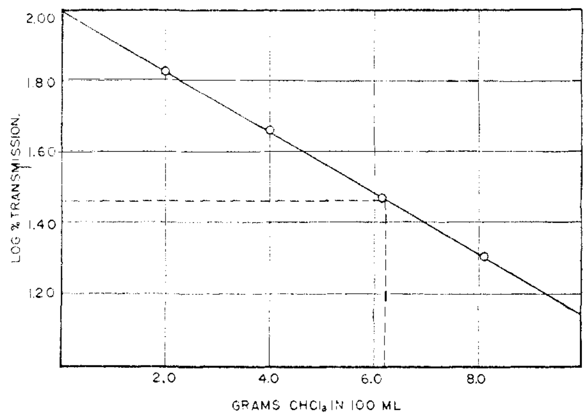

Fig. 3.—Infrared analysis, $CHCl_3$ in $CDCl_3$.

Summary

1. Chloroform-*d* has been prepared in good yield by the action of deuterium oxide on anhydrous calcium trichloroacetate.

2. The infrared absorption spectrum of the product has been measured and the purity quantitatively determined both by this means and by the density increment.

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(6) G. Emschwiller and J. Lecomte, *J. phys.*, **8**, 130 (1937).

[Contribution from the Illinois Institute of Technology and the National Bureau of Standards]

Investigation of the Deuterohaloform Synthesis.[1a] A New Preparation of Chloroform-*d*

By W. M. Boyer,[1b] R. B. Bernstein, T. L. Brown and V. H. Dibeler[1c]

The preparation of isotopically pure deuterohalomethanes is of considerable interest. This paper describes an investigation of the deuterohaloform synthesis and reports a new method for the preparation of chloroform-*d*.

Two of the deuterohaloforms, $CDCl_3$ and $CDBr_3$, have been reported previously.[2-5] These authors, however, made no systematic study of the factors influencing the isotopic purity of their products which were reported to contain the protium-bearing analog in significant, but, in most cases, undetermined amounts. In the present work, mass spectrometric, infrared spectrophotometric and density methods were employed for deuterium analyses in a quantitative investigation of this effect.

Experimental

High vacuum techniques were used in most of the chemical manipulations. A conventional vacuum apparatus was employed.

Chloral (Eastman Kodak Co. White Label), purified by distillation, was further dried by distilling through a heated

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(1) (a) Abstracted from the M.S. Thesis of W. M. Boyer; (b) Wallace A. Erickson & Co., 842 N. Wells, Chicago 10, Illinois; (c) National Bureau of Standards.

(2) F. W. Breuer, This Journal, **57**, 2236 (1935).

(3) T. W. Newton and G. K. Rollefson, *J. Chem. Phys.*, **17**, 718 (1949).

(4) (a) O. Redlich and F. Pordes. *Monatsh.*, **67**, 203 (1936); (b) O. Redlich and W. Stricks, *ibid.*, **67**, 328 (1936).

(5) R. Truchet, *Compt. rend.*, **202**, 1997 (1936).