

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Tetrachloroethane-1,2- d_2 (*sym*-Dideuteriotetrachloroethane)

BY FRITZ W. BREUER

Studies on organic compounds of deuterium, in progress in this Laboratory,¹ have been extended to the chlorination of acetylene- d_2 to give *sym*-dideuteriotetrachloroethane. A well controlled combination of the gases was effected by a negative catalyst. In common with other deuterium compounds the difference in density (d^{20}_4) 1.6118 as compared with 1.5943 for ordinary *sym*-tetrachloroethane, prepared in precisely the same way in the same apparatus, is most pronounced. Assuming the same molecular volume for the "light" and "heavy" compound the calculated density is 1.6136. The boiling point is about 0.5° higher than that of the ordinary compound, and it was found that the vapor pressures differ considerably.² Refractive indices (n^{20}_D) of the deuterio and known compounds are 1.4824 and 1.4940, respectively. In the Raman spectrum³ all lines predicted for the new substance are actually observed. The observation of Urey and Price⁴ of the slow interaction of aluminum carbide and deuterium oxide finds its analog in the low rate of evolution of "heavy" acetylene from calcium carbide. In the catalyzed reaction of ordinary and deuterio-acetylene with chlorine no appreciable difference in rates was noticed.

Experimental Part

Most of the methods described for the synthesis of *sym*-tetrachloroethane were tested for their suitability to small scale preparations involving the least risk of explosions. Finally the industrially used procedure utilizing the combination of acetylene and chlorine on a freshly prepared deposit of certain metal chlorides on a carrier was chosen. It was worked out carefully using ordinary water first.

Apparatus and Procedure.—The general assembly of the apparatus is shown diagrammatically in Fig. 1. The principal parts are an acetylene generating flask (a) with dropping funnel (a'), a storage system of four 500-ml. bulbs (b, b', b'', b''') interconnected by three-way

stopcocks, and using redistilled mercury as a confining liquid, a leveling bulb with customary air trap; two reaction tubes (c, c') made of heavy-walled (bomb) tubing, diameter 15 mm, length 15 and 30 cm., respectively, with cap joint for the gas inlets and standard tapered⁵ glass joint for the attachment of receivers (d, d') of the conventional type for the immersion in a cooling bath, and a terminal bubble counter (e). The all-glass chlorine purifying train consisted of a platinized asbestos-manganese dioxide catalyzer tube, heated electrically to 450°, gas wash bottles containing saturated potassium permanganate solution and concd. sulfuric acid, a pressure regulator (f) for the adjustment of the gas velocity and a capillary flow control with bubble counter (g). The catalyst, a mixture of 7.5 parts of ferric oxide, 7.5 parts of reduced iron, 15 parts of aluminum oxide, 5.5 parts of antimony metal (powdered) and 15 parts of clean quartz sand, which components had been either ignited or dried *in vacuo* at 110°, was suspended on ignited asbestos and packed rather loosely in the reaction tubes. They were wrapped with wire gauze and after attaching to the assembly the formation of the metal chlorides was started by a slow stream of chlorine. Part of the more volatile chlorides was expelled.

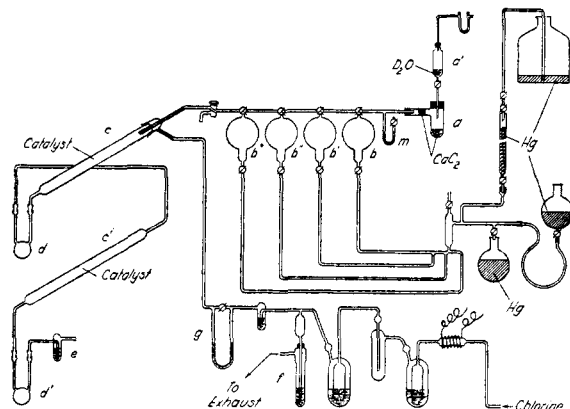


Fig. 1.

A constant and controllable rate of acetylene from the storage flasks to the reaction tubes was secured by a device consisting of a 12-liter carbony, filled with a 7-cm. layer of redistilled clean mercury and a heavy walled siphon tube with a set of two capillary stopcocks for the adjustment and shutting of the mercury flow.

Especially pure calcium carbide kindly supplied by Carbide and Carbon Chemicals Corporation, a light brown material, was crushed with exclusion of moisture and the inner cores powdered in an atmosphere of dry nitrogen. Generator (a) was charged with 8 g. (0.13 mole) of carbide and covered with a 3-mm. layer of ignited quartz sand. In the side-arm a layer of powdered calcium carbide was se-

(1) (a) Whitmore and co-workers, *THIS JOURNAL*, **56**, 749 (1934); (b) Breuer, *ibid.*, **57**, 2236 (1935).

(2) Cf. Lewis and MacDonald, *ibid.*, **55**, 3057 (1933), and Taylor and Junger, *ibid.*, **55**, 5057 (1933), for an explanation of vapor pressure differences of protium and deuterium compounds.

(3) To be published elsewhere by D. H. Rank of the Physics Department of the Pennsylvania State College.

(4) Urey and Price, *J. Chem. Phys.*, **2**, 300 (1934).

(5) See *Ind. Eng. Chem., News Edition*, **10**, 268 (1932).

cured between plugs of glass wool. The thoroughly dried acetylene generating and storage part of the system was outgassed most carefully through three-way stopcock (u), heating the carbide to 250°. Four cc. (0.22 mole) of deuterium oxide (d^{20}_4) 1.1071 was placed in dropping funnel (a') and permitted to react slowly with the carbide. Formation of "heavy" acetylene and the simultaneous removal of mercury from the storage bulbs were controlled so that the gas pressure was kept close to atmospheric, as indicated by manometer (m). Deuterium oxide was added in small portions whenever no change in pressure was noted during one-half hour. After sixty hours all of the "heavy" water had reacted, while the same volume of ordinary water had been used up in very considerably less time. Unreacted deuterium oxide was expelled by heating the generator to an oil-bath temperature of 170°, and brought into reaction with fresh carbide in the side arm. By simultaneously cooling the bulbs (b, etc.) with dry ice and keeping the generator at 170° most of the gas was transferred in the storage system and a nearly theoretical yield of acetylene- d_2 was obtained.

For the chlorination process a 100-watt incandescent bulb with metal reflector was placed at a distance of approximately 40 cm. from the reaction tube (c) and 16 cc. of chlorine per minute passed through the tubes prior to admitting the acetylene at a rate of 4 cc. per minute. Combination of the gases started immediately as indicated by the warming of tube (c) and the formation of a liquid reaction product. As a matter of precaution tube (c') was heated slightly by the flame of a wing-top burner. Very little gas passed through the terminal bubble counter (e), until the acetylene storage flasks were emptied (fifteen hours). The reaction products were expelled completely in receiver (d), which was kept at -10°, by repeated heating of tube (c) in a stream of chlorine, finally to the sublimation temperature of ferric chloride. No material had formed in reaction tube (c'). A yield of 14.5 g. of tetrachloroethane-1,2- d_2 (78% of the theoretical amount, based on deuterium oxide) was obtained.

Purification and Physical Constants.—Receiver (d) was attached by standard tapered glass joint to the pot of a partial reflux type fractionating column (length of packed⁶ section 37 cm., inner diameter 0.7 cm.) with sealed on pot and

multiple receiver, and transferred at 60 mm. pressure. Using a reflux ratio of 10:1 two fractions boiling at 68.8–70.7°, and 70.7° were collected, and the latter refractionated at 89 mm. to give three cuts with boiling ranges of 77.5–79.5°, 79.5–80° and 80°. From the middle fraction (8.5 g.) the density, boiling point, melting range and refractive index were determined by a technique described in an earlier paper.^{1b}

	CDCl ₂ CDCl ₂	CHCl ₂ CHCl ₂
d^{20}_4	1.6118	1.5943
n^{20}_D	1.4924	1.4940
B. p., °C. (737 mm.)	145.7 ± 0.05	145.2 ± 0.05

The melting curves of both deuterio and ordinary compounds indicate that these substances are not quite pure; nevertheless it was found that the "heavy" compound melts 0.2–0.5° higher than its protio analog. Preliminary measurements of vapor pressure differences of the "light" and "heavy" compound, taken at 5° intervals over the range +20–80° indicate that the vapor pressure of the deuterio compound is from 9–6% lower.

Grateful acknowledgment is made to the Carbide and Carbon Chemicals Corporation for the very pure sample of calcium carbide and to Dr. D. H. Rank of the Physics Department of The Pennsylvania State College for the permission to mention some of his as yet unpublished results. Particular thanks are due Dean Frank C. Whitmore of the School of Chemistry and Physics who made possible and greatly encouraged the present work.

Summary

Tetrachloroethane-1,2- d_2 has been prepared and some of its physical constants have been determined.

(6) Wilson and others, *THIS JOURNAL*, **55**, 2795 (1933).