107. *Preparation of Tetradeuteroethylene Dibromide by Direct Union of Dideuteroacetylene and Deuterium Bromide. A Route to Tetradeuteroethylene.*

By CHRISTOPHER L. WILSON and ALAN W. WYLIE.

A mixture of isomeric dibromotetradeuteroethanes containing about 10% of ethylidene dibromide has been made by passing deuterium bromide and dideuteroacetylene over a prepared charcoal catalyst at 180°. The best sample contained 99·7 atom % of deuterium. Details of the reaction with zinc to give tetradeuteroethylene are described.

An all-glass apparatus for the production of a continuous supply of up to 6 l. per hour of pure deuterium bromide by the combination of electrolytic deuterium with bromine has been designed.

THE ultimate object of the present work was a spectrographic study of tetradeuteroethylene. This project was largely forestalled by de Hemptinne, Jungers, and Delfosse (*J. Chem. Physics*, 1938, **6**, 319; cf. also de Hemptinne and Velghe, *Physica*, 1938, **5**, 958), who prepared a highly deuterated ethylene by a process essentially similar to ours and measured its long-wave spectra. These authors did not, however, directly determine the isotopic purity of their products. We have done this with our preparation and the process which we now describe would appear to provide material of exceptionally high isotopic purity. Our optical investigations have been indefinitely delayed.

Preparation of Deuterated Ethylene.—Deuterium was first introduced into the ethylene molecule by exchange between ethylene and deuterium over a nickel catalyst (Farkas,

Farkas, and Rideal, *Proc. Roy. Soc.*, 1934, *A*, **146**, 630). The simultaneous occurrence of a hydrogenation reaction would appear to preclude the use of this reaction for preparative purposes even though exchange predominates at high temperatures. Rather similar behaviour is found with a platinum catalyst (Farkas and Farkas, *J. Amer. Chem. Soc.*, 1938, **60**, 22). Horiuti and Polanyi (*Trans. Faraday Soc.*, 1934, **30**, 1164) observed exchange between ethylene and 2·7% " heavy " water, using platinum and nickel catalysts, and de Hemptinne *et al.* (*loc. cit.*) used this method to prepare mixtures of partly deuterated ethylenes. For their more highly deuterated material these authors combined dideuteroacetylene and deuterium bromide under the influence of ultra-violet light, and then removed the bromine from the resulting dibromoethanes by means of zinc. Dideuteroacetylene and deuterium bromide were made by reaction of calcium carbide and phosphorus pentabromide respectively with deuterium oxide. Direct isotopic analysis was, apparently, not attempted with either the dibromo-compound or the resulting ethylene, but the spectrographic results led these authors to conclude that their tetradeuteroethylene contained " a few per cent. of C_2HD_3." Mizushima, Morino, and Sugiura (*Proc. Imp. Acad. Tokyo*, 1938, **14**, 250) used mercuric bromide to catalyse the union of dideuteroacetylene and deuterium bromide; although they recorded spectral frequencies for the dibromo-compound produced, yet they neither determined isotopic composition nor were, apparently, aware that the product they handled was almost certainly a mixture of the αα- and the αβ-isomer. Since spectrographic results have but little value unless associated with a knowledge of purity, we have been careful to determine chemical and isotopic purity at all stages.

In some preliminary but unsuccessful experiments we attempted to realise exchange between ethylene and " heavy " sulphuric acid. Deuteration did occur, but only, apparently, through the formation and decomposition of ethyl hydrogen sulphate. Recovery of ethylene was very poor (cf. Ingold and Wilson, *Z. Elektrochem.*, 1938, **44**, 68). Decarboxylation of anhydrous salts of ethylenetetracarboxylic acid in the presence of metal deuteroxides was also tried. Here, simple decarboxylation was not realised but, instead, a complex reaction involving evolution of carbon monoxide occurred.

Union of Acetylene and Hydrogen Bromide.—Attention was then turned to reactions involving the addition of acetylene and hydrogen bromide which other workers have found practicable. For exploratory experiments the " light " forms of these molecules were prepared by reaction of carbide with water and the combination of electrolytic hydrogen with bromine. These particular methods of preparation and the apparatus used were designed primarily to permit easy and economical adaptation to deuterium work.

Failure attended attempts to unite acetylene and hydrogen bromide under pressure in Carius tubes (cf. Maas and Russell, *J. Amer. Chem. Soc.*, 1918, **40**, 1561). However, the large technical literature which has grown up around this problem since vinyl halides became important substances in the plastics industry would suggest that the reaction needs a suitable catalyst. Thus, de Hemptinne, Jungers, and Delfosse (*loc. cit.*) employed ultra-violet radiation (see U.S.P. 1,414,852, 1922). The addition of oxidising gases such as nitrogen dioxide has been claimed to facilitate the formation of vinyl halides (G.P. 368,467, 1919; U.S.P. 1,540,748, 1922). At elevated temperatures various metallic halides supported on suitable inert materials have been found satisfactory (B.P. 492,980, 1937; 339,093, 1929; G.P. 278,249, 1912). Even charcoal alone, if it is first activated by phosphoric acid (B.P. 339,727, 1929; U.S.P. 1,903,894, 1933) or hydrogen halide (B.P. 349,017, 1930), has been claimed to catalyse the addition.

We had but little success with metallic halides (*e.g.*, mercuric or ferric bromide) supported on various carriers, and it was not until we had noticed that spongy platinum became very active for the addition process only after a layer of carbon had formed on it by pyrolytic decomposition of acetylene that we tried activated charcoals. These proved very successful. The best results were obtained by activating granular charcoal in a stream of hydrogen bromide at 450° before the addition reaction was carried out at about 200°. Yields of up to 70% were realised, the product being mainly αβ-dibromoethane together with a few units % of the αα-isomer, vinyl bromide, and, surprisingly enough, ethyl bromide, the last probably formed as the result of a hydrogenation reaction. There is other evidence

(Tschitschibabin, *J. Inst. Pet. Tech.*, 1916, **3**, 48) that active charcoal can behave as a hydrogenation catalyst.

Although raising the temperature of reaction increased the yield of vinyl bromide, it is not clear why the major product at 200° was the dibromide, whereas the literature would have led one to expect vinyl bromide. Wibaut, however, showed (*Z. Elektrochem.*, 1929, **35**, 602; *Rec. Trav. chim.*, 1931, **50**, 311; Wibaut and van Dalfsen, *ibid.*, 1934, **53**, 489) that inert contact materials such as glass-wool, which failed to promote combination of acetylene and hydrogen bromide, were able to catalyse the union of vinyl bromide and hydrogen bromide. In the present experiments it may have been that the walls of the glass reaction tube acted in this way.

When a change over to deuterium compounds was made, it was found necessary, first, to replace exchangeable protium in the catalyst by deuterium. This protium could not be removed by heating to 500° under reduced pressure. Exchange was conveniently carried out by prolonging the activation process using deuterium bromide at 450°. Reaction of 2 mols. of deuterium bromide with dideuteroacetylene occurred best at 180° and led to a mixture of products similar in composition to that from the earlier experiments with "light" materials. In this way isomeric dibromotetradeuteroethanes, trideuterovinyl bromide, and pentadeuteroethyl bromide were prepared, the last two substances only in small amount. In all, some 250 g. of mixed dibromoethanes were made with the deuterium content of various samples ranging from 98·3 to 99·7 atom-%. The highest figure was represented by 93 g. of material.

Pure $\alpha\beta$-dibromoethane was prepared from the mixed isomers by reaction with zinc in moist (D_2O) dioxan and subsequent combination of the ethylene evolved with bromine. Absence of hydrogen exchange during this cycle of operations is rendered very probable by the work of other authors already referred to. We have not carried out isotopic analyses on these materials to check this conclusion.

The conversion of ethylene dibromide into ethylene oxide, sulphide, and imine is described in the literature. Our experience in this field confirms the low yields obtained except in the case of the oxide. In this instance we failed completely even to isolate the oxide by reaction of the dibromide with silver oxide in sealed tubes at temperatures up to 250° (cf. Greene, *Compt. rend.*, 1877, **85**, 624; 1878, **86**, 1141).

EXPERIMENTAL.

The general plan of the apparatus was as follows. Sections which may be described as the hydrogen bromide and the acetylene generator each delivered their products at predetermined rates into the catalyst tube. Here combination of the gases occurred and the organic bromo-compounds were collected in suitable traps. The entire apparatus was of glass, and standard joints and taps were used only where essential. Care was taken to search for pin-holes in the Pyrex seals, and the entire apparatus when assembled was evacuated and warmed to expel "light" moisture before deuterium compounds were introduced.

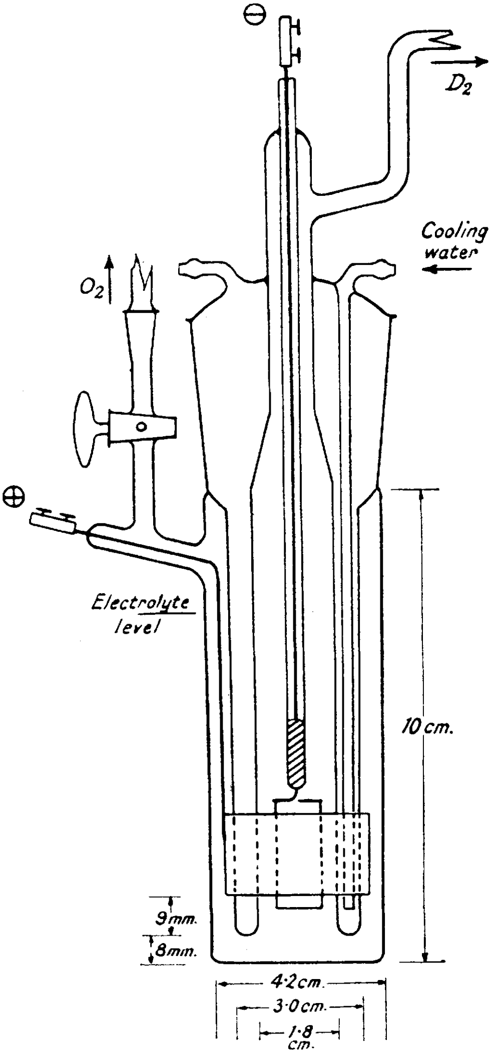
Electrolytic Deuterium Cell.—The deuterium generator, shown in Fig. 1, was made out of a large standard joint, the male portion of which was fashioned into a cylindrical water-cooled jacket surrounding the cathode. The cell had an electrolyte capacity of 60 c.c., and with 25% sulphuric acid a current of 5 amp. (corresponding to 2 l. of hydrogen per hour) could be passed without much rise in temperature; even at 8 amp. heating was not serious. The cylindrical platinum electrodes were made by welding foil and wire (approx. 18 S.W.G.) together. The rest of the apparatus offered a little back pressure to the flow of hydrogen and this was balanced by inserting a sulphuric acid bubbler, in the oxygen outlet. The pressure compensation could be varied by tilting the bubbler. Attachment to the oxygen outlet was made by thin lead tubing sealed with de Khotinsky cement, since rubber quickly deteriorated under the action of the ozone generated.

Deuterium Bromide.—Combination of deuterium and bromine was carried out in the apparatus shown in Fig. 2. Deuterium from the electrolysis cell was passed first through a trap at −78° to dry it and then through bromine kept at 48°. Reserve bromine was stored in the dropping funnel so constructed that it avoided the use of tap grease. "AnalaR" bromine was further purified by distillation from phosphoric oxide in a vacuum in an all-glass apparatus. The tap immediately preceding the bromine vessel was lubricated with phosphoric acid–graphite and sealed with mercury.

Mixed deuterium and bromine then passed on to the combustion chamber made out of a length of Jena " Supremax " combustion tube : this glass can readily be sealed to Pyrex. The chamber was filled with pieces of porcelain and wound with nichrome wire so that the first portion could be kept at about 80° and the second at 700°. After complete combination of the gases had been achieved the major part of any excess bromine was removed by a trap in liquid ammonia and the last traces by a column of copper turnings, previously washed with light petroleum and dried *in situ*.

FIG. 1.

Deuterium generator.



Under the conditions described, with a flow of deuterium of 2 l./hr., the yield of deuterium bromide was almost quantitative. Less than 1% (by vol.) of uncombined deuterium was present.

Acetylene.—The acetylene generator consisted of a 500-c.c. flask fitted with a graduated dropping funnel, the stem of which had been drawn out into a fine capillary. Water was dropped slowly and regularly on to calcium carbide, spread on copper gauze, and covered with a layer of pure dry dioxan, at a rate sufficient to evolve about 2 l. of acetylene per hour.

Commercial carbide was broken into pieces about the size of a pea and non-corroded fragments were selected for drying by ignition at 500° at 0·01 mm. The treated carbide was transferred directly to the flask without contact with atmospheric moisture. Dioxan (B.D.H. pure) was dried by refluxing over molten sodium for 5 hours before being distilled into the flask. The function of the copper gauze (30 mesh) was to allow the sludge to fall away from the carbide during reaction.

The acetylene, after passage through two traps at −78° to remove dioxan and water, and, incidentally, much of the other hydride impurities (hydrogen sulphide, arsine), was led through a calibrated flow meter containing coloured butyl phthalate as indicator liquid. Further control of the rate of gas flow was effected by a mercury-sealed gasometer connected to the gas line immediately prior to the flow meter.

The Catalyst Tube.—Acetylene and hydrogen bromide were thoroughly mixed by passage through a short column of glass wool before entry into the catalyst chamber. This consisted of a Pyrex tube 70 cm. long and 2·2 cm. in diameter wound with nichrome wire (28 S.W.G.) and well lagged with asbestos paper. The temperature could be varied between 100° and 500° by means of a series resistance. Sealed coaxially into the catalyst tube was a narrow glass tube which served as a thermometer pocket.

The products of reaction were passed through two collecting traps. The first, cooled in liquid ammonia, separated the bromo-compounds, and the second, in carbon dioxide–acetone, served to condense unreacted hydrogen bromide.

Catalyst.—Preliminary experiments are outlined on p. 597. For our main experiments we used active charcoal as described in B.P. 349,017. Both " Norit " and the more convenient granular variety (B.D.H. " Special for Gas Analysis ") were used, and were equally active. After being heated to 500° in a high vacuum for some time, the catalyst was activated at 450°

in a stream of hydrogen bromide. It was then ready for the addition reaction. When deuterium bromide was used, however, it was found that the gas issuing from the catalyst tube was seriously depleted of deuterium: this was due to an exchange process which had occurred with the protium present in the charcoal. The progress of this exchange is indicated in the following table.

Exchange of Hydrogen Fixed in Active Charcoal.

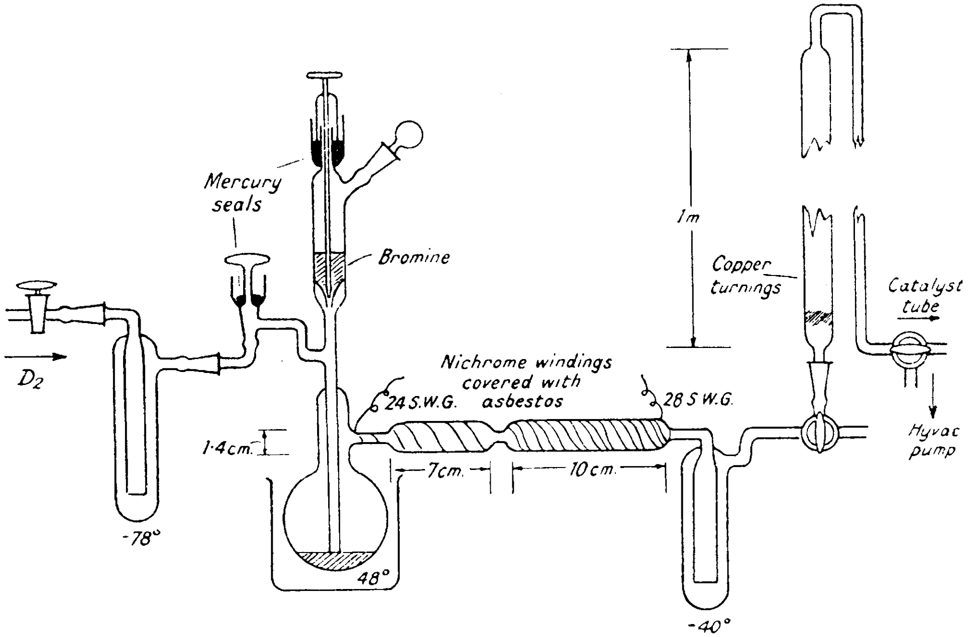
(Rate of flow of deuterium bromide, 4·0 l./hour; temp. 450°.)

Duration of expt. (mins.)	60	120	120	60	65	65	180	180	195
HBr evolved (atom-% of D) ...	0	12·0	46·3	57·9	79·9	90·7	97·4	99·3	(100·6)

At the beginning of the experiments represented, the electrolyte in the deuterium generator was made from 99·6% deuterium oxide. A separation coefficient of about 5 for the isotopes being assumed, the gas evolved would contain about 97·5% of deuterium. After the sixth experiment, however, when the electrolyte was reduced to about half, the gas evolved would have a deuterium content of 99·9%. Thereafter the cell was topped with 99·98% water.

FIG. 2.

Deuterium bromide generator.



Hydrogen bromide was analysed for deuterium in the following manner. The issuing gases, after passing through a trap immersed in liquid ammonia, were absorbed in a few c.c. of water in a second trap. The resulting aqueous solution was then analysed for bromine by precipitation as silver bromide, and for deuterium by distillation from excess of dry silver oxide in a vacuum, followed by density determination on the water. This technique has been described before. In calculating the results, allowance must be made for the replacement of bromine by its equivalent of oxygen when the solution is treated with silver oxide (cf. Nevell, de Salas, and Wilson, J., 1939, 1189).

Synthesis of Dibromoethanes.—(a) *Experiments with "light" materials.* In one of a series of exploratory experiments "Norit" activated charcoal, pre-treated by heating for one hour at 320° in a stream of hydrogen bromide, was used. Acetylene was generated at 1·8 l./hour and hydrogen bromide at 4·0 l./hour. After 5·25 hours at a reaction temperature of 220°, 44 g. (65%) of dibromoethanes had collected, together with 14 g. of a product, the bulk of which boiled at 35—45°. When the reaction temperature was raised to 300—350°, only the low-boiling product was obtained.

The dibromoethane sample was divided into two fractions, b. p. 110—127° and 127—131°. The latter on analysis gave C, 12·1; H, 2·11; Br, 84·9 (calc. for $C_2H_4Br_2$: C, 12·8; H, 2·12;

Br, 88·1%). From Wibaut's data (*Rec. Trav. chim.*, 1931, **50**, 311) for the freezing point and refractive index of mixtures of αα- and αβ-dibromoethanes, the first fraction, which should be the richer in the αα-isomer, was found to contain only 6·7% of this compound. This appeared to be very satisfactory. It was desirable that the content of αα-dibromoethane should be a minimum, since experiment showed that, when dissolved in alcohol or moist dioxan, it failed to react with zinc, whereas the αβ-isomer rapidly evolved ethylene.

The amount of vinyl chloride in the low-boiling fraction was estimated as follows. Hydrogen bromide (8 g.) was condensed on to 5 g. of the sample in a Carius tube cooled to −78°. The tube was sealed and then kept at room temperature in the dark for 48 hours, under which conditions vinyl bromide is converted quantitatively into dibromo-compounds (Kharasch, McNab and Mayo, *J. Amer. Chem. Soc.*, 1933, **55**, 2521). After separation of excess hydrogen bromide, the residue was found to boil over about the same range as before, and only 0·5 g. of product, b. p. 100—130°, was obtained. The amount of vinyl halide present would seem, therefore, to be less than 10% of the low-boiling fraction. The material, b. p. 35—45°, left after the hydrogen bromide treatment was shown to be largely ethyl bromide by conversion into β-naphthyl ethyl ether; this, after recrystallisation from petrol, had m. p. 35°. The amount of free hydrogen in the hydrogen bromide (less than 1%) was insufficient to account for the formation of almost 14 g. of ethyl bromide; hence it must be concluded that some of the acetylene is decomposed.

(b) *Experiments with deuterium compounds.* The results of some experiments are collected in the following table. Before deuterium analysis the material was treated with potassium carbonate and distilled many times in a vacuum. The data for deuterium content were the result of determinations on several different fractions of the high-boiling material. The individual figures agreed very well with one another.

Results of Three Experiments to prepare Deuterated Ethylene Dibromide.

(DBr, 4·0 l./hour; C_2D_2, 1·8—2·0 l./hour. Activation temperature, 450°. Deuterium oxide used, 99·98%.)

Activation period (hrs.).	Reaction temp.	Duration of expt. (hrs.).	Dibromoethanes.			Low-boiling product (g.).
			Yield.		D content	
			G.	% (on C_2D_2).	(D atom-%).	
1·25	180°	11	121	69·9	98·3	10
0·5	180—190	5	20	31·3	99·3	3
1·5	180	8	93	68·4	99·7	10

Isotopic Analysis.—About 0·2 g. of the purified dibromotetradeuteroethane was mixed with about 10 g. of highly purified "light" ethylene dibromide (b. p. 131·45—131·65°/760 mm., $n_D^{25°}$ 1·5355), and the mixture burnt over red-hot copper oxide in a stream of dry air (cf. Ingold, Raisin, and Wilson, J., 1936, 914). The combustion water was purified, and its density determined in the usual manner. Deuterium content of the dibromoethane was calculated from the formula

$$D = [F_0(1 + H/L) - 0{\cdot}00017]/(H/L - nF/M)$$

where D is the atom-fraction of deuterium in the hydrogen of the dibromoethane, F the atomic fraction of deuterium in the combustion water in excess of that in tap water, $F_0(= F + 0{\cdot}00017)$ the absolute value of F (0·00017 corresponds with the deuterium content of tap water used as density standard), $n(= 4)$ the number of atoms of hydrogen per molecule in the substance burnt, M the molecular weight of the protium compound, and H and L the weights (g.) of the deutero- and the protio-compounds respectively. The equation is general for mixtures of such molecules.

Preparation of Tetradeuteroethylene and Pure Tetradeuteroëthylene Dibromide.—The mixed deuterö-bromides were dissolved in purified dioxan to which one drop of deuterium oxide had been added. One molecular proportion of zinc was added, and the mixture warmed. Evolution of ethylene was rapid. It was passed through traps at − 78° to free it from dioxan and then into cooled traps containing purified bromine. Excess bromine was removed by washing with aqueous sulphur dioxide, and the product dried over phosphoric oxide and distilled in a vacuum.

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THE SIR WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON.

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