[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF COLUMBIA UNIVERSITY]

Deutero-acetaldehyde (Acetaldehyde-d_4)

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The synthesis of acetaldehyde-d_4 by the hydration of acetylene-d_2 appeared to the writers as a desirable method of approach to the organic chemistry of deuterium inasmuch as the reacting materials were easily obtainable and the reaction lent itself to being carried out in a closed system.

The hydration of acetylene-d_2 with deuterium oxide was first attempted in the vapor phase by passing acetylene-d_2 and deuterium oxide vapor over a tungsten oxide catalyst at 400° but the copious formation of polymerization products made this method unsuitable for working with a comparatively expensive material. The absorption of acetylene by a deuterium oxide solution of phosphoric acid in the presence of mercuric sulfate was finally adopted and found to work very satisfactorily.

Deutero-acetaldehyde and the corresponding polymerization product, deutero-paraldehyde were thus obtained in a reasonably pure state. A preliminary notice of this work has already been published.[1]

The product obtained does not appear to differ chemically from ordinary acetaldehyde although there remains the question as to whether the reactions exhibited are due to the deutero-aldehyde group—CD=O or to an ordinary aldehyde group formed by an interchange reaction either with the solvent or the reagent. Until a set of pure deuterium reagents becomes available or it can be definitely established that such an interchange does not occur, that question cannot be answered.

The physical properties are, however, definitely changed. The densities, particularly, are considerably increased. It is to be noted that the molecular volumes—as far as they can be determined by comparing densities at equal temperatures—remain constant. The melting points of both the deutero-acetaldehyde and the corresponding paraldehyde are distinctly higher but there is little difference in the boiling points.

The Raman spectrum as determined by Professor R. W. Wood of Johns Hopkins University[2] showed the expected shift in lines.

For purposes of comparison the physical constants of acetaldehyde and of deutero-acetaldehyde are given together in Table I.

Experimental Part

Materials.—As the calcium carbide of commerce contains considerable amounts of calcium hydroxide which by exchange reactions would contaminate the deutero-acetylene made from it, the calcium carbide used in these experiments was made in an induction furnace by heating to 1800–2000° precipitated calcium carbonate mixed in proper proportions with thermatomic carbon (carbon from the thermal decomposition of natural gas). The carbonate had but traces of sulfate and no phosphate that could be detected. There were no mineral impurities in the carbon used. The crucibles were made by boring out 3″ (7.6 cm.) graphite electrodes. Every precaution was taken to prevent contamination of the carbide, which was kept in glass-stoppered bottles sealed with paraffin. The carbide for this and other experiments was made in small batches of about 250 g. as needed so as to avoid keeping any of it over long periods.

The deuterium oxide was procured from Rjukan, Norway, and was redistilled and checked for purity by the interferometer method.[3] It analyzed 99.6% deuterium oxide.

Apparatus.—In order to avoid as much as possible contamination with moisture from the air the synthesis was carried out in a closed system made entirely of Pyrex glass. The apparatus, Fig. 1, consisted of a generator A into which the carbide was dropped through a side tube and the deuterium oxide dropped on it from a small separatory funnel. The deutero-acetylene was collected over mercury in the reservoirs B and B′ each holding about one liter and from there passed into the absorption vessel C which during the reaction was shaken vigorously. This was permitted by a glass spiral in the gas line. The shaking machine was operated by a small motor D provided with an eccentric.

Operation.—About 1 g. of dry mercuric sulfate was placed in the absorption vessel. A tube containing approximately the amount of phosphorus pentoxide was sealed to one of the side tubes of the absorption vessel, the entire apparatus exhausted to dry it as completely as possible and, after letting in dry air, 25 to 30 g. of phosphorus pentoxide was volatilized into the reaction vessel in a current of dry oxygen.

A tube containing 25 g. of deuterium oxide was then sealed in and the water distilled into the reaction vessel under a pressure of less than 1 mm. Every precaution was taken at all times to prevent not only contamination with moisture from the air but with moisture from the oxygen torch employed in sealing. Stopcocks were suitably arranged so that any moisture formed could be pumped out without coming in contact with the reaction materials. The absorbing solution consisted then of a 40–50% deutero-

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[1] THIS JOURNAL, **57**, 2735 (1935).

[2] A discussion of this matter will be the subject of a separate communication by Professor Wood.

[3] Crist, Murphy and Urey, *J. Chem. Phys.*, **2**, 112 (1932).

phosphoric acid in deuterium oxide with 1 g. of mercuric sulfate as catalyzer. Acetylene-d_2 was then led in from one of the reservoirs, the other being used as storage for the acetylene that continued to be evolved after the deuterium oxide had been turned off. Vigorous shaking greatly facilitated the reaction.

The absorption was rapid at first, as much as 1 liter of acetylene-d_2 being absorbed in twenty minutes, but the rate gradually diminished to about 1 liter an hour. When acetylene ceased to be absorbed, the apparatus was connected with a cooling system and the contents of the vessel distilled under reduced pressure at room temperature, except toward the end when gentle heat was applied. Dissolved acetylene-d_2, acetaldehyde-d_4, deuterium oxide and paraldehyde-d_{12} came over and had to be fractionated. The fractionation was carried out entirely under a pressure of a fraction of a millimeter, using solid carbon dioxide–acetone and liquid air for obtaining the desired temperatures. Some 50 g. of the acetaldehyde and 6 g. of the paraldehyde were thus prepared.

The residue in the reaction vessel consisting of phosphoric acid, polymerization products and compounds of mercury was treated with anhydrous sodium carbonate and potassium permanganate to recover the deuterium as deuterium oxide. The residue of calcium deuteroxide from the acetylene generator was distilled at 700–800° and the deuterium oxide recovered.

Deutero-acetaldehyde.—After numerous fractionations deutero-acetaldehyde was obtained as a water white mobile liquid with a sharp odor and burning taste. The physical constants are given in Table I. Chemically it behaves, as far as could be determined, as ordinary acetaldehyde. It reduces ammoniacal silver oxide, restores the color to a fuchsine–sulfur dioxide solution and gives crystalline compounds with ammonia (small white cubes, m. p. 92–94°, dec.) and with sodium bisulfite. It resinifies when heated with alkalies.

About 2 g. was burned over copper oxide in a current of oxygen and the recovered water analyzed by the interferometer method showing 99.2% pure D_2O. This means that despite all precautions about 0.4% of ordinary water must have entered into the reaction and contaminated the deuterium.

The tendency of the acetaldehyde to polymerize is present in the deutero compound particularly after exposure to the air. Appreciable amounts of deutero-paraldehyde were found when sealed tubes in which the aldehyde was kept were opened after standing for some weeks.

Deutero-paraldehyde.—One of the fractions of the reaction consisted of deutero-paraldehyde and deuterium oxide. The same relation appears to exist between these two as between paraldehyde and water. The solubility of the paraldehyde decreases with increasing temperature. The paraldehyde layer which floated on top of the deuterium oxide was separated, dried with "drierite" and fractionally distilled. The paraldehyde was obtained as a water white oily liquid with a mint-like odor and a cooling taste. The physical properties are given in Table I. When solidified below 13°, the paraldehyde crystallizes in long prismatic needles.

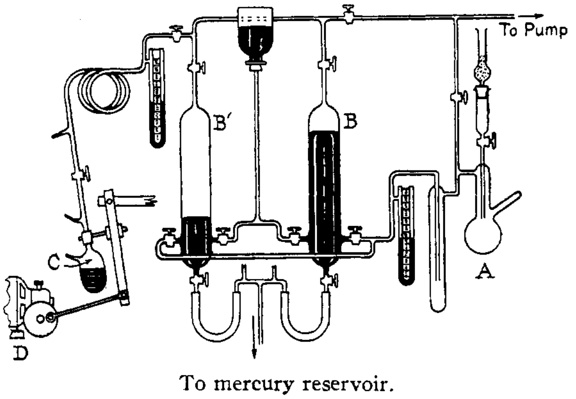

Fig. 1.

A microanalysis gave: C, 50.1, 50.3; D, 16.3, 16.5. Calcd. for $(C_2D_4O)_3$: C, 50.0; D, 16.7.

TABLE I

	Acetaldehyde	Acetaldehyde-d_4
B. p., °C.	20.2 (1 atm.)	20.5 (756 mm.)
M. p., °C.	−123.5	−121.7
D^0_0	0.806[4]	0.883
V. p., 0°C.	331 mm.[4]	327 mm.
	Paraldehyde	Paraldehyde-d_{12}
B. p., °C.	124 (1 atm.)	124–125 (753 mm.)
M. p., °C.	10.5	13.7
d^{20}_{20}	0.994	1.078

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Summary

Acetaldehyde-d_4 and paraldehyde-d_{12} were obtained by the action of acetylene-d_2 on deuterium oxide and their properties reported.

Further work on these compounds is now in progress in this Laboratory.

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[4] Gilmour, *J. Soc. Chem. Ind.*, **41**, 293 (1922).