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Preparation of Benzene-d_6 by Polymerization of Acetylene-d_2

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Dedicated to Professor *Ole Lamm* on his 60th birthday

A water-cooled reaction tube with a centered heating rod electrically heated to about 700°C has been used for the preparation of benzene-d_6 by polymerization of acetylene-d_2. A specially constructed generator is charged with calcium carbide and heavy water is supplied dropwise at a rate corresponding to an acetylene-d_2 production of about 6 l per hour. After some purification, the acetylene-d_2 is fed to the reaction tube and the reaction products formed condense on the cold walls and are collected in a small tube below and parallel to the reaction tube. One third by weight of the raw product is benzene-d_6. After the reaction is completed, the generator is heated to about 600°C which decomposes the calcium hydroxide-d_2 so that the excess water is completely recovered. The yield of benzene-d_6 calculated from the heavy water consumed is about 20 %. The deuterium content of the product lies near that of the heavy water used. The apparatus has also been used for preparation of benzene containing tritium.

Several methods concerning the preparation of benzene-d_6 have been described. They are based on catalyzed hydrogen-deuterium exchange in benzene [1–4] or on polymerization of acetylene-d_2 [4–6]. Only some of these are suitable for preparation on a larger scale, *e.g.*, the method of Brüllman, Gerber and Meier [3] where the deuterium exchange between deuterium chloride and benzene is utilized.

The preparation of benzene-d_6 by polymerization of acetylene-d_2 can be performed by heating acetylene-d_2 to about 600°C in a tube [5]. One difficulty is that the reaction heat liberated by the polymerization creates local hot areas with the resulting formation of higher polymers and coal-like substances. In addition, the conditions for formation of benzene-d_6 are unfavourable from a thermodynamical point of view; naphthalene-d_{10}, for instance, is more likely to be formed [7]. However, by using a reaction vessel with a high temperature gradient, it is possible to reduce these problems. In such a reaction vessel, the "lighter" products formed rapidly diffuse from the hot to the cold zone

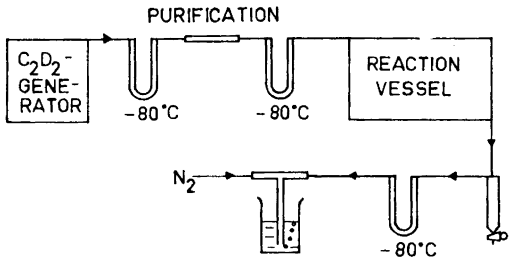

Fig. 1. Flow scheme.

and are thus protected from further reaction. This principle has been utilized for the preparation of benzene by polymerization of acetylene [8], and for the preparation of naphthalene-d_{10} by polymerization of acetylene-d_2[7]. The present method utilizes the principle for the preparation of benzene-d_6.

APPARATUS

The flow scheme shown in Fig. 1 has been used. The specially constructed generator is charged with calcium carbide, and heavy water is supplied dropwise at a rate corresponding to an acetylene-d_2 production of about 6 l per hour. After passing a cold trap, a purification tube [7] containing a mixture of 46 % copper oxide, 46 % manganese dioxide and 8 % silver oxide *, and a second cold trap, the acetylene-d_2 is fed to a slightly inclined reaction vessel consisting of a water-cooled reaction tube with a centered heating rod electrically heated to about 700°C. The reaction proceeds quite calmly and continuously. The reaction products condense on the cold wall of the reaction tube and flow down into a thinner tube parallel to and below the reaction tube. From the reaction vessel, the dark-red liquid flows into a collecting flask from which it can be withdrawn through a stopcock. Gases which do not condense in the cold trap placed after the collecting flask leave the system through a water lock consisting of a T-tube, one arm of which dips down 3—4 cm in water. A slow stream of nitrogen is supplied to the third arm of the T-tube, which maintains a slight over-pressure in the apparatus.

The generator

Acetylene-d_2 has been prepared by many investigators [4–7,9] from calcium carbide and heavy water. In order to get a high yield one utilizes the fact that calcium hydroxide-d_2 gives off water upon heating to about 600°C. From a practical point of view there are some difficulties with the methods generally employed. The moist calcium hydroxide-d_2 formed has a tendency to enclose carbide particles which prevents complete reaction in a reasonable time. By heating this mixture to 600°C, heavy water is liberated and reacts with the carbide particles giving acetylene-d_2. The acetylene-d_2, however, decomposes

* Caution: use of a high concentration of silver oxide can result in explosion.

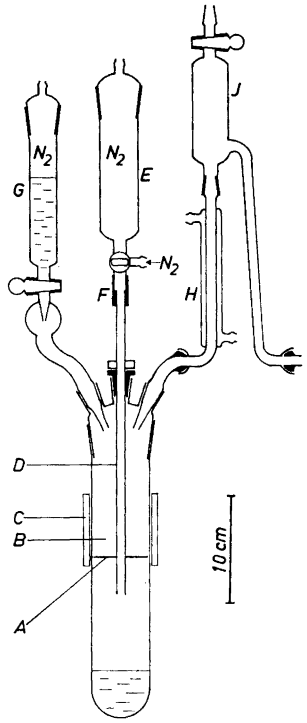

Fig. 2. Acetylene-d_2 generator. A, stainless steel plate; B, carbide; C, electrical element; D, stainless steel tube; E, G, container for heavy water; F, three-way stopcock; H, cooler; J, container which together with H can be bent down at the ball-joints.

in the mixture with mainly coal and deuterium as a result. This problem is eliminated with the generator shown in Fig. 2. As is seen, the generator is supplied with an extra bottom (A) on which lies the carbide (B) heated to about 100°C with an electrical element (C) outside the generator tube. This bottom, which consists of a round stainless steel plate perforated with holes of 3 mm diameter, is attached to a stainless steel tube (D) which fits through a gas-tight Teflon plug at the top of the generator. On the real bottom of the quartz generator tube lies heavy water supplied from the container (E) through the three-way stopcock (F) and the tube (D). The heavy water is allowed to flow into the generator only after all the air in the apparatus has been swept out by nitrogen, also supplied through the stopcock (F). By dropping heavy water from the container (G), acetylene-d_2 and calcium hydroxide-d_2 are formed. The acetylene-d_2 escapes through the cooler (H) where most of the heavy water which follows it condenses and drops back down onto the carbide. The calcium hydroxide-d_2, which exists as a dry white powder as a result of the heating, passes the carbide bed and falls together with small carbide particles down into the heavy water in excess on the real bottom of the generator where the carbide particles react completely. To get a continuous transport through the carbide bed and thus continuous acetylene-d_2 production, one can use a vibrator or some device on the outside attached to the stainless steel tube (D) to periodically swing the tube (D) and the upper bottom through a small

angle. It is also advisable to cool the outside of the real generator bottom with ice water to prevent the reaction heat liberated there from volatilizing the heavy water. When all the carbide has been transformed into calcium hydroxide-d_2 on the real bottom of the generator, this bottom is heated to about 600°C. The heavy water liberated condenses in the cooler (H) which is now bent down at the ball joint and the heavy water is finally collected in the container (J). A practically complete yield is achieved.

The reaction vessel

The reaction vessel used is shown in Fig. 3. A water cooler (K) made of Pyrex glass cools the reaction tube (L) and a small collecting tube (M) connected to the latter by several equidistant short cross-tubes. This unit, which is made of Vycor glass, is tightly held in place by rubber plugs (N) at the ends of the cooler. (It is advisable to use some rubber glue to achieve complete tightness and rigidity). At the center of the reaction tube sits a heating rod (O) made of a quartz tube with an inner heating spiral in a nitrogen atmosphere which heats the rod to about 700°C. The quartz tube is held in place at the ends of the reaction tube by gas-tight Teflon plugs (P). The left plug also holds the inlet (Q) for acetylene-d_2.

The collecting tube contains a device consisting of a movable stainless steel rod (S) with a knob (R) and with Teflon membranes attached at the same intervals as the cross-tubes mentioned above. (Every membrane is held in place between two small nuts on the screwed rod). The membranes, when in a position away from the openings of the cross-tubes, fit tightly to the walls of the collecting tube thus preventing gases, mainly acetylene-d_2, from escaping the reaction tube. The main reaction occurs at the left end of the reaction tube where the acetylene-d_2 is supplied. This is concluded from the fact that the heating rod is hotter (is more light-red) in this area because of the heat liberated by the reaction. Also at this end, the fumes and gases can be seen to circulate between the reaction tube and the collecting tube. This occurs because of the inclination of the tube (about 1:10) and the influence of the temperature gradient. The reaction products condense on the walls of the reaction and the collecting tubes and are finally automatically collected in the latter as a dark-

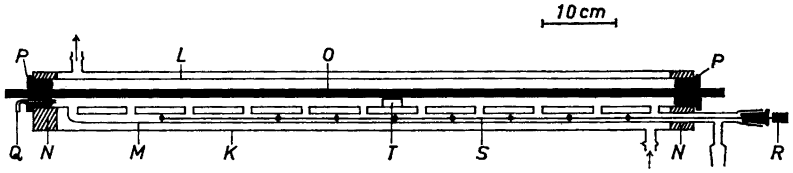

Fig. 3. Reaction vessel for polymerization of acetylene-d_2 to benzene-d_6. K, water cooler made of Pyrex glass; L, reaction tube connected to the collecting tube M by equidistant cross-tubes, the unit is made of Vycor glass; N, rubber plug; O, heating rod; P, gas-tight Teflon plug; Q, inlet for acetylene-d_2; R, knob for displacing the insert S; T, quartz support for O.
The reaction vessel is slightly inclined to the right.

red, clear liquid. By displacing the insert (S) in the collecting tube so that the Teflon membranes come just in front of the crosstubes, the product is allowed to flow out into the collecting flask described earlier.

EXPERIMENTAL

For an 8 h experiment the generator is charged with 80 g of calcium carbide previously heated to about 600°C to decompose the calcium hydroxide on the surface of the carbide pieces. The container (G) (Fig. 2) is supplied with 25 g of heavy water, the container (E) with 25—50 g. The three-way stopcock (F) is then opened for nitrogen for about 20 min so that all the air in the apparatus is swept out. Then the stopcock is turned so that all the heavy water in the container (E) is transferred to the bottom of the generator. Now heavy water is supplied dropwise from the container (G) at a rate corresponding to an acetylene-d_2 production of about 6 l per hour. In the reaction tube, the heating rod, if new, will be covered with a thin layer of coal when acetylene-d_2 first is introduced. This coal layer seems to have a catalyzing effect. If the supply of acetylene-d_2 is irregular or too high, the acetylene-d_2 concentration near the heating rod will be so high that a direct decomposition into coal and deuterium will occur [7,10]. This appears as a flame wandering some centimeters along the heating rod giving rolling veils of coal attached to the heating rod. The phenomenon slightly diminishes the yield, but on the other hand because of the catalyzing effect of the veils, it increases the capacity of the reaction tube. When the preparation is completed, after about 4 h, the excess heavy water in the generator is driven off by heating to about 600°C as described above. The heavy water thus recovered is used for filling the container (E) of the generator in the next run and so on. The raw product is distilled for benzene-d_6.

Table 1 shows the yields of four successive runs, each starting from 80 g of pre-heated technical calcium carbide. This amount of carbide theoretically should consume 25.4 g of heavy water corresponding to 35.5 g of benzene-d_6.

The fresh heavy water used contained 99.78 atom % deuterium in the hydrogen. The deuterium content measurements were made with a proton magnetic resonance method [11].

Table 1. Results from four successive runs.

Run	D_2O-consumed (g)	Generator-yield (%)	Amount rawproduct (g)	Amount C_6D_6 received (g)	Yield of C_6D_6 (%)	Deuterium-content of the product (atom %)
1	25.4	100.0	21.8	~7	~20	99.50
2	25.0	98.4	21.5	~7	~20	—
3	25.5	100.3	Break because of mishap		—	—
4	24.9	98.0	21.7	~7	~20	99.40

The deuterium content of the heavy water recovered after the forth run had decreased to 99.60 atom %.

DISCUSSION

As described above, one third by weight of the raw product is benzene-d_6 corresponding to a yield of about 20 %. The residue has not been thoroughly investigated but it contains toluene-d_8, naphthalene-d_{10} and many other aromatic substances which can be of interest in themselves. However, by burning this residue in oxygen to heavy water, it should be possible to increase the net yield of benzene-d_6 to about 50 %.

As is shown in Table 1 the deuterium content of the product is about 0.3 atom % lower than that of the heavy water used. This is mainly due to the method used here in charging the generator with carbide. The previously dehydrated carbide was poured from its container into the generator and could react with moisture in the air during this procedure. The thin but invisible layer of calcium hydroxide thus formed contributes in later reactions to the light hydrogen content of the product and of the heavy water recovered. This contamination can be avoided if the carbide is pre-heated to 600°C *inside* the generator under slow passage of nitrogen to withdraw the light water liberated. Thereafter, generation of acetylene-d_2 will give the maximum deuterium content [6]. The net yield of benzene-d_2 increases with the purity of the acetylene-d_2 because of a decreased tendency to side reactions. Especially pure carbide has thus been used by some workers [4]. On the other hand, the purification described above seems to be effective, and further purification has failed to increase the yield.

Starting from acetylene containing other isotopes of hydrogen and/or carbon it is possible to use the apparatus for the preparation of products containing these isotopes. Thus the apparatus has been utilized for preparing benzene containing tritium starting from calcium carbide and water containing tritium.

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