

## Synthesis of Greatly Enriched HD

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The maximum concentration of the hydrogen-deuterium molecule HD which can be obtained in the equilibrium mixture is approximately 50%. The equilibrium constant for the reaction  $H_2 + D_2 = 2HD$  has been determined (5, 12) and is near 4, which would be expected from random distribution of the three molecular species.

In making studies of the boron hydrides, I have found a method by which HD of 85% concentration can readily be prepared. The residual gases are  $H_2$  and  $D_2$ .

The synthesis consists in direct complete deuteration of  $B_2H_6$  by  $D_2$ , and slow reaction of the  $B_2D_6$  with  $H_2O$ , producing HD. The reactions were followed and the gases analyzed by a mass spectrometer operated as has been described (11).

One other note of direct synthesis of HD was found. H. Beutler *et al.* (2) reacted LiH with D<sub>2</sub>O, and used the ultraviolet absorption between 750 and 850 A to determine H<sub>2</sub>, D<sub>2</sub>, and HD. They report enrichment in HD above the equilibrium amount.

The first step in the  $B_2H_6$  method is deuteration using  $D_2$  gas obtained from the Isotopes Branch, U. S. Atomic Energy Commission. The deuteration proceeds slowly at room temperature, in a pyrex bulb, without catalyst. Equilibrium is attained in  $1\frac{1}{2}$  hr at 80° C, with only a

FIG. 3. A longitudinal section through part of a muscle fiber. Regions adjacent to I and A correspond to isotropic and anisotropic bands. Order in particle arrangement is best preserved in regions enclosed by the inked-in circle. Magnification,  $\times 27,250$ .

section, demonstrates that there is three-dimensional, and by definition crystalline, order in the arrangement of the macromolecular components of the fibrils of this striated muscle. The regularity is most pronounced in the anisotropic bands.

An awareness of this high degree of order in its structure is obviously important for an understanding of muscle and of the way it functions. We are continuing this investigation to find out more about the nature and fine structure of the particles which display this order and to see how they are changed by muscular contraction.

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small amount of thermal decomposition of the  $B_2H_6$ . Successive amounts of  $D_2$  must be added, for the deuteration at each stage is only partial. This is due to the accumulation of  $H_2$  removed from the  $B_2H_6$  molecule in the process. After each stage in the deuteration, liquid  $N_2$  was used to condense the  $B_2H_6$ - $B_2D_c$ , the  $H_2$ diluted  $D_2$  was pumped away, and fresh pure  $D_2$  was added. About seven stages, with large excess pressure of  $D_3$  over  $B_2H_6$  in each, produces  $B_2D_6$  of purity greater than 95%, and further additions of pure  $D_2$  give no further change in the mass spectrum of the  $B_2D_6$ .

The progress of deuteration was followed by the mass spectrometer. At complete deuteration, the ratio of mass peaks 32 to 31 is very close to 2.0. These peaks represent the ions B<sup>11</sup>B<sup>11</sup>D<sub>5</sub> and B<sup>10</sup>B<sup>11</sup>D<sub>5</sub>. These values are to be expected from an abundance ratio of boron B<sup>11</sup>/B<sup>10</sup> = 4.0. This is in agreement with the value found at the National Bureau of Standards (4). The ratio of the parent ion, B<sup>11</sup>B<sup>11</sup>D<sub>6</sub> at mass 34 to the ion B<sup>11</sup>B<sup>11</sup>D<sub>5</sub> at mass 32 was found to be under 1%, even smaller than is the case with the parent ion for normal B<sub>2</sub>H<sub>6</sub> and B<sub>2</sub><sup>10</sup>H<sub>6</sub> (3, 11).

The second step in producing highly enriched HD is to react the pure  $B_2D_6$  slowly with low concentration of  $H_2O$  over  $H_2SO_4$ , at 25° C.

Into a 63-cc pyrex bulb, 5 ml of  $H_2SO_4$ , sp. gr. 1.752 (20° C) was placed. This is 82.8%  $H_2SO_4$ . It produces a water vapor pressure of about 0.03 mm at 25° C. The mass spectrometer showed no detectable  $SO_2$  or  $SO_3$  in the gas phase at this temperature. The acid was degassed by alternate freezing and thawing, and pure  $B_2D_6$  con-



FIG. 1. Mass spectra before and after equilibration by heating on Ni filament. A, B, 50–50 mixture of  $H_2$  and  $D_2$ . C, D, synthesized HD, initially 85%.

densed in the bulb by liquid  $N_2$ . The bulb was closed and warmed to 25° C.

The pressure in the bulb was 30 mm to start. In one day at 25° C it became 40 mm and in 4 days 70 mm. The amount of  $B_2D_6$  at the end of this time was 22 mm, and with it was 48 mm of a gas not condensable by liquid nitrogen. This was found to be greatly enriched HD.

HD of high concentration above equilibrium should be capable of being broken down to the equilibrium mixture, just as mixtures of  $H_2$  and  $D_2$  can be brought up to the equilibrium ( $\delta$ ). This was done, and the results of heating with a nickel filament are shown in Fig. 1, where the mass spectra of various mixtures are shown for the main mass peaks 2, 3, and 4.

The mass spectra were obtained as follows. Maximum focus for each of the peaks from 1 (for H<sup>+</sup>) to 6 (for  $D_{a}^{+}$  molecular ion) was first ascertained. Then a magnetic scan was made, with 2000 volts accelerating, 70 volts ionizing. Calibrations were made with pure H<sub>2</sub>,  $D_{2}$ , and known mixtures. A precise time schedule for gas admission and scanning was followed, identical for each analysis. This tended to cancel out or minimize any differential pumping effects (7). The scan was such that before each peak came up the adjustment for maximum focus could be made. The whole procedure yielded sensitivity relationships such as were found by Honig (8).

Fig. 1, Section A, shows the spectrum of a mixture of  $H_2$  and  $D_2$ . The gas consisted of 45%  $H_2$ , 8% HD, and 47%  $D_2$ . On heating by a nickel filament at about 600° C, this equilibrated to give 30%  $H_2$ , 48% HD, and 22%  $D_2$  (Fig. 1, Section B). The equilibrium constant found was K = 3.5.

The gas obtained by slow hydrolysis of  $B_2D_6$  with  $H_2O$ , after the  $B_2D_6$  and  $H_2O$  were condensed out by liquid nitrogen, gave the mass spectrum in Fig. 1, Section C. This gas was 85% HD, 8%  $H_2$ , and 7%  $D_2$ . After equilibrating by the hot filament this gas had the mass spectrum of Fig. 1, Section D, and the composition was 32% H<sub>2</sub>, 48% HD, and 20% D<sub>2</sub>, with K=3.6. The values of K tabulated by Jones (9) give 3.87 at  $627^{\circ}$  C and 3.26 at  $25^{\circ}$  C.

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That the reaction with water is the main event occurring is shown by mass spectra of  $B_2D_6$  taken as the reaction proceeds. The 32/31 peak ratio went from 2.0 to 1.75, the rest of the spectrum remaining almost the same. This represents a relatively small amount of dedeuteration, since this ratio is very sensitive to departures from completely deuterated  $B_2D_6$  composition. The fact that peak 32 does not represent adventitious oxygen is assured by the good resolution afforded by the spectrometer. This can resolve (10) the portions of peak 32 due to  $O_2$  and due to  $B_2{}^{n}D_5$  ion. No oxygen was found in this investigation.

The chemical equations for steps in this method are:

$$B_2H_6 + 3D_2 = B_2D_6 + 3H_2 \tag{1}$$

$$B_2D_6 + 3H_2O = B_2O_3 + 6HD.$$
 (2)

A naive picture for step (2) is to consider the terminal D atoms on the B as  $B \swarrow_D^D$  and  $O \swarrow_H^H$  the water molecule fitting into the < in this manner: <<. This brings the O close to the B for reaction and the H and D in close contact to form HD. The concept seems less speculative if we recall (1) that in  $B_2H_6$  the angle corresponding to  $B \bigtriangledown_D^D$  is 120°, and the angle in  $O \backsim_H^H$ is 105°. The interatomic distances, if  $B_2D_6$  resembles  $B_2H_6$ , would be B - D = 1.18 A and O - H = 0.96 A. The dimensions are not inconsistent with this concept.

Extension of this simple picture leads to an explanation of why a maximum of 85% HD was attained. The bridge structure for diborane now seems well substantiated (1, 6). In the deuterated  $B_2D_6$  the two central bonding D atoms are in an angular configuration different from the terminal D atoms, and in a plane at 90°:



If the four terminal deuteriums react as suggested, 4HD will be produced. If now the two central deuteriums are left to react with HOH *purely statistically*, there will be formed an additional  $\frac{1}{2}(H_2 + 2HD + D_2)$ . The final result is  $5HD + \frac{1}{2}H_2 + \frac{1}{2}D_2 = 83.3\%$  HD + 8.35% $H_2 + 8.35\%$  D<sub>2</sub>. These figures are nearly those observed. Paul Zemany of our laboratory suggested this last result.

The over-all reaction may be written  $B_2H_6 + 3D_2 + 3H_2O = 3H_2 \uparrow + B_2O_3 \downarrow + 5HD + \frac{1}{2}H_2 + \frac{1}{2}D_2$  where the  $3H_2$  is removed in step (1), the  $B_2D_6$  being held by liquid  $N_2$ , and the  $B_2O_3$  is removed in step (2) by deposition on the walls or in the acid, leaving behind a relatively pure HD.

The converse reaction of ordinary  $B_2H_6$  with  $D_2O$  vapor at room temperature was also found to give HI)

concentrations above equilibrium values, but the HD was less concentrated than that produced by the first method.

Wender, et al. (13) have prepared very pure HD by reacting  $D_2O$  with lithium aluminum hydride. Data for HD preparation by rectification of liquid  $H_2$ -HD- $D_2$  mixtures are given by Clusius and Starke (3a).

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# A Study of the Albumin and Globulin Content in Postpartum Plasma and Its Use in Rheumatoid Arthritis

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It was first reported from this clinic that a sustained remission can be produced in rheumatoid arthritis by the administration of suitable amounts of postpartum plasma (1). A review of the literature failed to reveal any data on the use of postpartum plasma in rheumatoid arthritis. The remission produced was characterized by an improved sense of well-being, a brighter mental outlook, increased

TABLE 1POSTPARTUM PLASMA PROTEINS (4)

Pool	Albumin mg %	Globulin mg %	Total protein mg%
1	2.1	2.8	4.9
<b>2</b>	2.1	2.2	4.3
3	2.7	1.8	4.5
4	2.4	2.3	4.7
5	2.0	2.1	4.1
6	2.1	2.6	4.7
7	2.1	2.0	4.1
8	2.5	1.6	4.1
9	1.7	2.4	4.1
10	1.9	2.1	4.0
11	2.2	2.3	4.5
12	2.0	2.2	4.2
Average	2.15	2.20	4.35

appetite, a disappearance of joint symptoms, a gain in weight, restoration to normal of the microcytic anemia and albumin globulin ratio. In general, the characteristic response was a striking clinical improvement. There were no toxic effects, and in 320 postpartum plasma transfusions there were no cases of homologous serum hepatitis. The longest remission following cessation of therapy was 16 weeks and the shortest was 3 weeks. Postpartum plasma is an available and comparatively inexpensive form of therapy. During the investigation the author noted that the postpartum plasma had a greenish tint, slightly opalescent and homogeneously distributed.

Table 1 reports the albumin and globulin content of the plasma obtained from 96 mothers after delivery. Each pool represents the pooled plasma of eight mothers.

Despite the hypoproteinemia, the mothers from whom this plasma was taken presented no anemia or edema. The typical average protein value was 4.35 mg % with an albumin globulin ratio of 0.9. The lack of correlation between plasma protein levels and edema was striking. A marked hypoalbuminemia was also observed and yet no impaired hepatic or renal function could be demonstrated. The postpartum plasma proteins reported here apparently resemble the pattern noted in the maternal sera at or near term (3). This similarity may provide an explanation for the efficacy of postpartum plasma in rheumatoid arthritis. The occurrence of pregnancy in patients with rheumatoid arthritis produces a partial or completeremission in a high percentage of cases (2).

At present there is no clear explanation of the ameliorating effect of postpartum plasma in the treatment of rheumatoid arthritis. There is suggestive evidence that this behavior is not due solely to a steroidal factor.

Further study of postpartum plasma will be reported.

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# The Action of Pectinase Solutions on Sections of Acetone-fixed Human Tissues: A Preliminary Note

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The action of enzymes on tissue sections is a source of chemical information. It has been found that solutions of diastase remove glycogen (5). The usefulness of the procedure is limited by impurity of the enzyme preparations and by complexity of the substrate (2, 6). This paper introduces commercial pectinase as an enzyme active on suitably fixed human tissues, and discusses the validity of the information derived from its use.

Thin pieces of human tissue are fixed in ice-cold ace-