# NOTES

## Concerning Edmonds and Birnbaum's Equation for the Equilibrium Constant for the Formation of a Colored Complex[1]

By Edward S. Amis

Edmonds and Birnbaum[2] from

$$\frac{y}{x} = \frac{\log I_y}{\log I_x} \tag{1}$$

obtained the equation

$$K = \frac{b^n d^n (\log I_y - \log I_x)}{d^n \log I_x - b^n \log I_y} \tag{2}$$

for the equilibrium constant, $K$, for the formation of colored complex. $I_x$ and $I_y$ were the light intensities transmitted by two solutions of concentrations $x$ and $y$ of colored complex when the second component had the respective concentrations $b$ and $d$, and $n$ was the number of moles of the second component uniting with one mole of the first component of concentration $a$ to give the colored complex.

Equation (2) is valid when $I_0$ is unity. In American-made optical instruments $I_0$ is not taken as unity but as 100 and the transmission $I/I_0$ is read in per cent. The expression for $y/x$ becomes

$$\frac{y}{x} = \frac{\log I_y/I_0}{\log I_x/I_0} \tag{3}$$

and the general equation for $K$ is then

$$K = \frac{b^n d^n (\log I_y - \log I_x)}{d^n \log I_x - b^n \log I_y + \log I_0 (b^n - d^n)} \tag{4}$$

and for $I_0 = 100$ we have

$$K = \frac{b^n d^n (\log I_y - \log I_x)}{d^n \log I_x - b^n \log I_y + 2(b^n - d^n)} \tag{5}$$

If $I_x$ and $I_y$ refer to fractions of transmitted light, equation (2) is correct. The symbol $I$, however, ordinarily represents intensity of light.

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[1] Work supported by the Office of Naval Research under contract with the Institute of Science and Technology of the University of Arkansas.

[2] S. M. Edmonds and N Birnbaum, This Journal, **63**, 1471 (1941).

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Received October 5, 1951

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## The Preparation and Characterization of Some Deuteroboron Compounds

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In relation to physical-structural studies on borine carbonyl[1] and dimethylaminodiborane,[2] it was necessary to employ the B-deuterated varieties for comparison purposes. Accordingly $B_2D_6$ was prepared and converted to the desired compounds. Some physical properties of these and incidental by-products are described in this note. It appears that the melting points and vapor tensions of most of the deutero-compounds differ enough from those of the protium compounds for use in assaying the results of tracer studies involving these substances.

**Pure $B_2H_6$.**—Diborane was prepared by the use of lithium aluminum hydride.[3] After a preliminary distillation in the high-vacuum apparatus at the lowest feasible temperature, it was purified by forming the unstable $(CH_3)_2OBH_3$ at −78.5°;[4] the impurities were pumped off at −100° and the diborane recovered from the decomposing complex by distillation through a trap at −150°. As a final step, the diborane was left for an hour at −78.5°, to form the complex from any remaining trace of methyl ether, and then distilled from a tube at −160°. This was the procedure which yielded the sample in which the mass-spectrograph showed no impurity.[5] The vapor tension at −111.9° was observed as 225.0 mm. (cor.).

**$B_2D_6$.**—Pure diborane was deuterated by successive treatments with samples of deuterium generated from 99.8% pure $D_2O$, until calculation indicated 98% replacement. Equilibrium at each stage was assured by heating the mixture in a previously baked-out Pyrex bulb for 24 hours at 75°—conditions far more energetic than those suggested by studies of the rate of exchange.[6] The 98% $B_2D_6$ had a vapor tension of 238.3 mm. (cor.) at −111.9°, in agreement with a private communication from H. I. Schlesinger and B. Rice.

**Pentaborane.**—Occasional overheating of the exchanging mixtures led to minor yields of deuterated pentaborane; a sample between $B_5H_2D_7$ and $B_5HD_8$ had a vapor tension of 67.5 mm. at 0°—definitely above the rechecked value of 66 mm. for $B_5H_9$.[7]

**$(CH_3)_2OBD_3$.**—It was noticed also that the methyl ether complex formed from 85% deuterated diborane had a dissociation pressure of 30 mm. at −78.5°; by comparison with the 18 mm. value for $(CH_3)_2OBH_3$,[4] this result would indicate 32 mm. for pure $(CH_3)_2OBD_3$ in equilibrium with $B_2D_6$ and $(CH_3)_2O$ at −78.5°. The 80% increase of dissociation pressure upon deuteration suggested the possibility of separating partially deuterated diborane into light and heavy fractions, since the reaction $B_2H_6 + 2(CH_3)_2O \rightarrow 2(CH_3)_2OBH_3$ would be most favored for the least deuterated material. In an actual test, a 75% deuterated sample of diborane was separated into 70 and 80% fractions by overnight treatment with an equal gas-volume of methyl ether at −78.5°, with recovery of the lighter half of the original sample by decomposition of the complex. However, such a process would become very tedious for purification of $B_2D_6$, since the absolute separation decreases sharply as the D-content increases.

**$(CH_3)_2ND$.**—Before $(CH_3)_2NB_2D_5$ could be prepared by the usual aminolysis,[8] it was necessary to prepare $(CH_3)_2ND$, since the use of $(CH_3)_2NH$ would have led to HD, and an exchange with the B–D bonds in the product would mean serious contamination. That such an exchange actually does occur under the preparative conditions was shown by heating a 22-cc. sample of $(CH_3)_2NB_2H_5$ with 115 cc. of $D_2$ (gases at S.C.) for 74 hours at 100°; then after repurification, the dimethylaminodiborane showed an increase of vapor tension from the original 101.2 to 103.8 mm. at 0°. Subsequent studies of nearly pure $(CH_3)_2NB_2D_5$ showed that this result corresponded to 65% deuteration (calcd., 67%). Accordingly, $(CH_3)_2ND$ was prepared by the room temperature reaction of $[(CH_3)_2N]_2BH$ with 99.8% $D_2O$. An exchange contamination of the product by the action of HD

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[1] W. Gordy, H. Ring and A. B. Burg, *Phys. Rev.*, **78**, 512 (1950).

[2] D. E. Mann and B. L. Crawford, Jr., unpublished.

[3] A. E. Finholt, A. C. Bond, Jr., and H. I. Schlesinger, This Journal, **69**, 1201 (1947).

[4] H. I. Schlesinger and A. B. Burg, *ibid.*, **60**, 296 (1938).

[5] V. H. Dibeler and F. L. Mohler, *ibid.*, **70**, 988 (1948).

[6] A. N. Webb, J. T. Neu and K. S. Pitzer, *J. Chem. Phys.*, **17**, 1007 (1949).

[7] A. Stock and W. Siecke, *Ber.*, **57B**, 570 (1924).

[8] A. B. Burg and C. L. Randolph, Jr., This Journal, **71**, 3452 (1949).